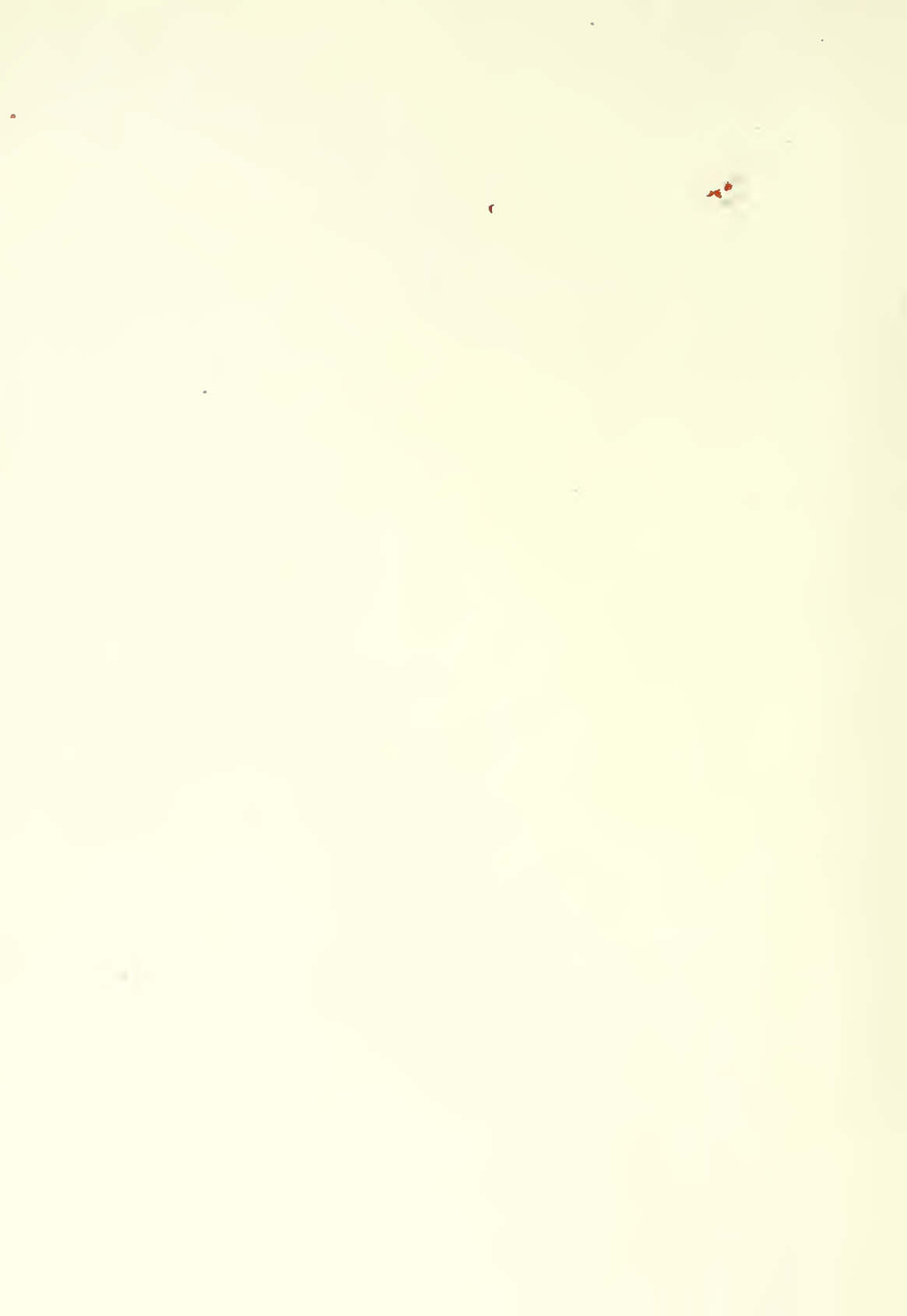
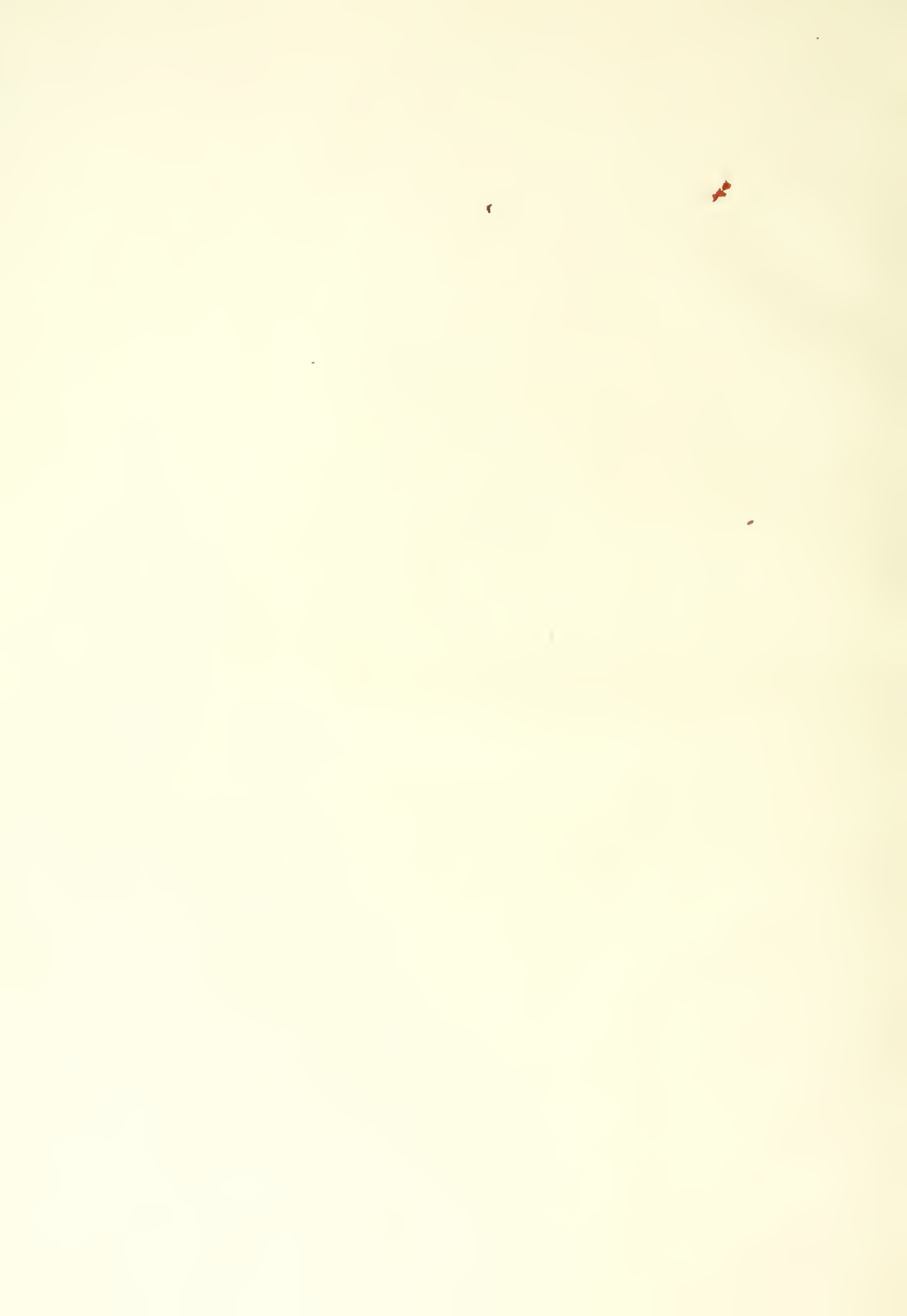


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THE CHEMICAL NEWS, JULY 28, 1916

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A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

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EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME CXIII.

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No. 2928.—JANUARY 7, 1916.

THE QUALITATIVE ANALYSIS OF THE IRON GROUP IN PRESENCE OF PHOSPHATES.

By ROBERT GILMOUR.

Two general methods for the separation of the metals of the iron group are in common use. In the first of these iron, aluminium, and chromium are separated as hydroxides by means of ammonia in the presence of ammonium chloride, and the filtrate is treated with ammonium sulphide, which precipitates the remainder of the metals of the group as sulphides. In the second method the metals are precipitated together as hydroxides and sulphides by the addition of ammonia, ammonium chloride, and ammonium sulphide. The subsequent isolation and identification of the constituent metals may then be effected by several methods, each of which possesses certain advantages, but all of which possess also serious disadvantages.

The separation of iron, chromium, and aluminium by precipitation with ammonia is never an entirely satisfactory process, since manganese is certain to be partially precipitated at the same time, unless a large excess of ammonium chloride is present, and even then oxidation of the manganese salt to the manganic state, through absorption of atmospheric oxygen and subsequent precipitation along with the iron, chromium, and aluminium, is sure to occur to some extent. Again, a considerable quantity of zinc may be precipitated if much chromium is present, and manganese, zinc, and nickel may all be carried down in presence of much iron (Noyes, *Journ. Am. Chem. Soc.*, 1908, xxx., 482). Furthermore, as will be shown later, magnesium may be carried down almost completely if much aluminium is present, unless a much larger amount of ammonium chloride has been added than is usual in qualitative analysis. With regard to the separation of the remaining metals of the groups, the chief difficulty is the solubility of nickel sulphide in yellow ammonium sulphide. This can be overcome, however, by precipitating with hydrogen sulphide in ammoniacal solution (*loc. cit.*).

When the metals are precipitated together as hydroxides and sulphides the above mentioned difficulties do not, of course, occur, except that magnesium may be precipitated in presence of much aluminium. When, however, we come to consider the further separation of the metallic radicles of this group fresh difficulties appear. Many textbooks recommend treatment of the precipitated hydroxides and sulphides with cold dilute hydrochloric acid in order to separate the insoluble nickel and cobalt sulphides from the remaining metals of the group, but this is far from satisfactory, for, as Thiel and Gessner have shown (*Zeit. Anorg. Chem.*, 1914, lxxvi., 1), nickel sulphide when

precipitated under ordinary qualitative conditions is soluble to a very considerable extent in 0.5N or even 0.1N hydrochloric acid, due to the probable existence of three distinct forms of the sulphide, which vary in solubility; consequently, the separation is very incomplete.

Another difficulty, which does not seem to have been mentioned in the literature, occurs when a phosphate is present along with metals of the alkaline earth group in the solution undergoing examination. In the usual analytical schemes iron and phosphate are separated together by the basic acetate process, leaving manganese, barium, strontium, calcium, and magnesium in solution, and also nickel and cobalt if these have not been separated previously. This process is not without its drawbacks, for it has been found that barium may be almost completely precipitated along with the ferric phosphate and basic ferric acetate, and strontium and calcium to a considerable extent. Consequently, if all the barium has come down with the iron group on account of a large amount of phosphate being present it may be missed altogether, since the ferric phosphate precipitate is generally neglected. This seems to add another charge to the already long list against the method of separating the alkaline earths as carbonates after the iron group, and constitutes another argument in favour of Curtmann and Marcus's method of separating them as sulphates after the silver group (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1493), or after the copper group as advocated in this paper. Certainly one or other of the methods must be adopted if the separation is to be at all exact, and it is largely a matter of choice which one, for on the one hand, if the sulphates are precipitated before the copper group it is necessary to treat them with ammonium acetate to remove lead, while on the other hand precipitation of the sulphates after removal of the copper group may result in a certain loss of barium, particularly if ferric chloride or other oxidising agent happens to be present. On the whole, the method of Curtmann and Marcus is perhaps to be preferred from the point of view of accuracy. Care must be taken, however, to make the separation of the sulphates as complete as possible by the addition of a considerable quantity of alcohol, for the scheme about to be described gives little further opportunity for the detection of the alkaline earth metals if a phosphate is present.

In consequence of the difficulties which have been referred to above an attempt has been made to devise a more satisfactory working method for the analysis of the iron group, and this has been more or less successfully accomplished.

The scheme taken in conjunction with those already advocated for the analysis of the copper and alkaline earth groups (CHEMICAL NEWS, 1915, cxi., 206 and 217) con-

stitutes a method for the complete analysis of a solution for the basic radicles.

Briefly the procedure is as follows:—

The solution from which the metals of the silver and copper groups have been eliminated is boiled to remove H_2S . The alkaline earths are then removed as sulphates by means of H_2SO_4 and alcohol. The precipitated sulphates are converted into carbonates and analysed according to the method previously described in this journal (*loc. cit.*).

The filtrate is heated on the water-bath for some time to remove alcohol, $NaOH$ is added, and then Na_2O_2 in considerable quantity. The mixture is boiled for some minutes and filtered. The filtrate contains aluminium, chromium, and zinc, and most of the phosphate if this is present. The precipitate contains $Fe(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$, $MnO(OH)_2$, $Co(OH)_3$, $Mg(OH)_2$, and phosphates of these. The filtrate is examined as usual for Al, Cr, and Zn. The precipitate is dissolved in HCl , and the solution evaporated to dryness. The residue is taken up in water, tested for iron, and Fe and phosphate removed by the basic acetate process. The filtrate contains Ni, Co, Mn, and Mg. It is heated to boiling, and H_2S is passed in. Ni and Co are precipitated as sulphides. The filtrate is made alkaline with NH_4OH , and H_2S again passed in; Mn is precipitated as sulphide. The filtrate on addition of $(NH_4)_2HPO_4$ gives Mg as $MgNH_4PO_4$.

Na and K are tested for in a portion of the original solution after removing all other metals by means of NH_4OH , NH_4Cl , H_2S , and $(NH_4)_2CO_3$.

PRELIMINARY EXPERIMENTS.

Action of $NaOH$ and Na_2O_2 on Solutions containing Al and Zn.

1. To a solution containing 56 mgrms. of Al and 64 mgrms. of Zn as chlorides, 2 cc. of 2/N $(NH_4)_2HPO_4$ were added, then $NaOH$ until the precipitate just dissolved. A pinch of Na_2O_2 was then added and the solution boiled. A white granular precipitate came down, which would not dissolve on continued boiling.

2. In a similar experiment, in which the Na_2O_2 was omitted, the same white granular precipitate was obtained.

3. Solutions containing 56 mgrms. of Al and 64 mgrms. of Zn were treated with $NaOH$ until clear. On boiling the solutions they remained clear, but on mixing them and boiling the white precipitate appeared.

4. 500 mgrms. of $ZnSO_4$, 500 mgrms. of $Al_2(SO_4)_3$, and 500 mgrms. of $(NH_4)_2HPO_4$ were dissolved in $NaOH$ solution. A quantity of Na_2O_2 was added and the solution boiled. Only a small amount of the white precipitate appeared.

A further series of experiments of a similar nature showed that if the amount of $NaOH$ or Na_2O_2 which was added was considerably in excess of that required to dissolve the precipitated hydroxides, then no insoluble substance was formed, whereas if only a sufficient amount was present to just dissolve the hydroxides when precipitated in separate solutions, or a very small excess over this amount, then on boiling the white precipitate was formed. This result would seem to point to the formation of some compound containing Zn and Al, possibly zinc aluminate, and on this assumption might be regarded as due to an equilibrium reaction, with $NaAlO_2$ and Na_2ZnO_2 on one side of the equation and zinc aluminate and $NaOH$ on the other side. An excess of $NaOH$ would thus tend to prevent the formation of the zinc aluminate, inasmuch as it would facilitate the ionisation of both zinc and aluminium hydroxides in the acid form.

The experiments show clearly, at any rate, that a considerable excess of Na_2O_2 is required in the peroxide separation of Al, Cr, and Zn, as otherwise appreciable quantities of Zn and Al may remain undissolved, along with CO, Ni, and the other metals of the group.

The Precipitation of Aluminium in presence of Magnesium by means of NH_4OH .

1. To a solution containing 56 mgrms. of Al as chloride and 48 mgrms. of Mg as sulphate in 30 cc. about 2 mgrms. of solid NH_4Cl were added, and then NH_4OH in slight excess. The mixture was boiled and filtered and the precipitate (a) well washed.

The filtrate gave on adding $(NH_4)_2HPO_4$ a precipitate of $MgNH_4PO_4$ (b).

The precipitate (a) was dissolved in dilute HCl , 1 grm. of NH_4Cl and excess of NH_4OH were then added and the mixture boiled.

The precipitate was filtered off and washed (c).

The filtrate gave a small precipitate with $(NH_4)_2HPO_4$.

Precipitate (c) still contained a considerable quantity of Mg, as evidenced by the $NaOH$ and iodine test.

2. 48 mgrms. of Mg as sulphate were precipitated as $MgNH_4PO_4$. The precipitate appeared to be about four to five times larger than the precipitate (b) in the last experiment.

Quantitative Experiments with Mg and Al.

1. A solution containing 56 mgrms. of Al and 50 mgrms. of Mg was diluted to 60 cc. 5 mgrms. of solid NH_4Cl were added, and then 2/N NH_4OH until the solution was alkaline (15 cc.). The mixture was boiled and filtered and the precipitate washed thoroughly with hot water. The Mg in the filtrate was estimated as $MgNH_4PO_4$.

$MgNH_4PO_4$ found .. = 0.2052 grm.
= 45 mgrms. of Mg

Mg originally present = 50 mgrms.

5 mgrms. of Mg therefore remain with the Al.

2. Al 56 mgrms., Mg 25 mgrms., NH_4Cl 5 mgrms., NH_4OH 15 cc.

The filtrate gave .. 0.1136 grms. of $MgNH_4PO_4$
.. = 24.8 mgrms. of Mg.

Mg present... .. = 25 mgrms.

In this case practically all the Mg has remained in solution.

3. Al 56 mgrms., Mg 50 mgrms., NH_4Cl 2 mgrms., NH_4OH 15 cc.

The filtrate gave .. 0.0770 grm. of $MgNH_4PO_4$
= 16.8 mgrms. of Mg.

Mg present... .. = 50 mgrms.

In this case 33 mgrms. of Mg have been precipitated with the Al.

It is evident from these experiments that the greater part of the Mg may be precipitated along with the Al (probably as magnesium aluminate) unless a very much larger excess of NH_4Cl is present than is usual in qualitative analysis. This would explain the frequent failure to detect Mg in an ordinary analysis.

The result is of course one which might be predicted from the fact that alkaline solutions favour the ionisation of aluminium hydroxide in the acid form. In all probability the solubility product constants of $Mg(OH)_2$, $Mg(AlO_2)_2$, and $Al(OH)_3$ decrease successively, in which case a concentration of OH' ion not sufficient to precipitate Mg alone as hydroxide might nevertheless in the presence of Al be sufficient to prevent the concentration of the AlO_2' ions falling below the value required by the solubility product $Mg \times (AlO_2')^2$. A further decrease in the OH' ion content, following on the addition of more NH_4Cl might then decrease the AlO_2' ion concentration sufficiently to bring the product $Mg \times (AlO_2')^2$ below the solubility coefficient value, and consequently Mg would remain in solution.

The Separation of Iron and the Alkaline Earth Metals in the Presence of Phosphates.

The procedure in the following series of experiments was in most cases substantially the same as in Experiment No. 1 below. One or two special cases are treated separately.

Fe and Ba.

1. A solution containing 112 mgrms. of Fe and 46 mgrms. of Ba as chlorides was treated with a few cc. of $(\text{NH}_4)_2\text{HPO}_4$ solution and then with dilute HCl until the precipitated phosphates just dissolved. Some solid $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and 2 cc. of 2/N acetic acid were then added and the solution diluted to 40 cc. and boiled. The precipitate was filtered off and washed well.

The filtrate gave a small precipitate of BaSO_4 on adding H_2SO_4 .

The precipitate of FePO_4 and basic ferric acetate was dissolved in dilute HCl and treated with a little H_2SO_4 . A precipitate of BaSO_4 was obtained roughly three to four times larger than that obtained from the filtrate.

2. Some FePO_4 was prepared by precipitation and thoroughly washed with hot water until practically free from chlorides. A portion of this was boiled with BaCl_2 solution for a few minutes, then filtered and washed with hot water until free from chlorides.

The filtrate gave a heavy precipitate of BaSO_4 on adding H_2SO_4 . The precipitate of FePO_4 on dissolving in dilute HCl and adding H_2SO_4 gave a small precipitate of BaSO_4 , not more than about one-tenth of that obtained from the filtrate.

3. Another portion of the FePO_4 was boiled up with a solution containing 46 mgrms. of Ba, 1 gm. of $\text{NaC}_2\text{H}_3\text{O}_2$ and a few drops of 2/N acetic acid. The precipitate was then filtered off and washed free from chlorides, dissolved in dilute HCl and tested with H_2SO_4 . A white precipitate of BaSO_4 was obtained.

The filtrate was treated with H_2SO_4 and gave a precipitate of BaSO_4 , roughly equal in amount to that obtained from the FePO_4 .

4. 56 mgrms. Fe, 46 mgrms. Ba, 2 cc. 2/N $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. 4/N acetic acid, and 6 cc. 2/N $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$.

FeCl_3 was added until the mixture was just yellow, after which the latter was boiled and the precipitate filtered off and washed. The filtrate gave a small precipitate of BaSO_4 . The precipitate of FePO_4 and basic ferric acetate on dissolving in HCl and adding H_2SO_4 gave a very much larger amount of BaSO_4 .

Practically all the Ba remained with the FePO_4 .

5. To a solution containing 56 mgrms. of Fe, 46 mgrms. of Ba, 1 cc. 4/N acetic acid, and 6 cc. 2/N $\text{NaC}_2\text{H}_3\text{O}_2$, 2 cc. of 2/N $(\text{NH}_4)_2\text{HPO}_4$ were added in the cold. The precipitate was filtered off and washed carefully with cold water. On testing for Ba the precipitate was found to contain much more of this than the filtrate.

6. 56 mgrms. of Fe were precipitated as basic ferric acetate in presence of 70 mgrms. of Ba. The precipitate was filtered off and washed well. On testing it for Ba only a trace was found, while the filtrate was found to contain practically all the Ba.

7. 56 mgrms. Fe, 115 mgrms. Ba, 7 cc. 0.5/N $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. 4/N acetic acid, and 8 cc. 2/N $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. FeCl_3 was added until the mixture was just yellow, and the latter was then boiled for five minutes and the precipitate filtered off and washed well. The filtrate and the precipitate contained about equal amounts of Ba.

(To be continued).

Reports follow on the conditions under which the last harvests of 1914-15 took place, and very complete tables show the production of cereals of this year in almost all Northern Hemisphere countries.

Including several modifications from the *Bulletin* of November, the total crops of each cereal are as follow:—

Wheat.—The crop for the following group of countries is officially estimated for 1915 at 989,740,769 quintals, against 826,607,938 in 1914, or 119.7 per cent of the latter amount:—Hungary, Bulgaria, Denmark, Spain, France, Great Britain and Ireland, Italy, Luxemburg, Norway, Netherlands, Roumania, Russia in Europe, Switzerland, Canada, United States, India, Japan, Russia in Asia, Egypt, and Tunis.

Rye.—For the following group of countries the 1915 crop is officially estimated at 300,522,512 quintals, against 261,796,607 in 1914, or 114.8 per cent:—Hungary, Bulgaria, Denmark, Spain, France, Ireland, Italy, Luxemburg, Norway, Netherlands, Roumania, Russia in Europe, Switzerland, Canada, United States, and Russia in Asia.

Barley.—The 1915 crop is officially estimated at 269,492,306 quintals, against 229,301,652 in 1914, or 117.5 per cent for the following group of countries:—Hungary, Bulgaria, Denmark, Spain, France, Great Britain and Ireland, Italy, Luxemburg, Norway, Netherlands, Roumania, Russia in Europe, Switzerland, Canada, United States, Japan, Russia in Asia, Egypt, and Tunis.

Oats.—The 1915 crop is officially estimated at 563,490,494 quintals, against 456,250,940 in 1914, or 123.5 per cent for the following group of countries:—Hungary, Bulgaria, Denmark, Spain, France, Great Britain and Ireland, Italy, Luxemburg, Norway, Netherlands, Roumania, Russia in Europe, Switzerland, Canada, United States, Russia in Asia, and Tunis.

Maize.—The 1915 crop is officially estimated at 909,654,237 quintals, against 802,317,332 in 1914, or 113.4 per cent for the following group of countries:—Hungary, Italy, Roumania, Russia in Europe, Switzerland, Canada, United States, Japan, and Russia in Asia.

In the *Bulletin* there follow next reports on the rice, flax, cotton, potato, hop, tobacco, vine olive, and sugar beet and cane crops. More particularly is to be noted among the new data published on these crops the production of potatoes in Ireland, viz., 37,695,981 quintals, or 107.7 per cent of the 1914 crop, and in France (90,570,920 quintals, or 75.5 per cent), and also the wine production of Roumania, viz., 1,670,980 hectolitres, or 250.6 per cent of that in 1914, and of France, where the partial results referring to the four principal Departments of the South (Hérault, Aude, Gard, and Eastern Pyrenees) give 9,556,840 hectolitres, or 32.4 per cent of the corresponding production in 1914.

The agricultural part of the *Bulletin* ends with data from the live-stock statistics of France collected at July 1, 1915, and at December 31, 1914.

The commercial part contains tables of imports and exports, stocks, and prices of cereals and cotton on the chief markets, the tables being as complete as possible under present conditions.

NITROGEN, CHLORINE, AND SULPHATES
IN RAIN AND SNOW.

By BONNIBAL ARTIS.

FROM October 12, 1914, to June 19, 1915, we continued the investigations made by Knox (CHEMICAL NEWS, xci., 61), investigating fifty-one samples. There were thirty-five precipitations of rain and sixteen of snow, or 15.35 inches of rain and 37.75 inches of snow, equivalent to 18.49 inches of rain.

The heaviest rainfall 1 inch, occurred May 20, and the largest amount of snow, 8 inches, fell on December 29. The largest amounts of sulphates were found during the

INTERNATIONAL INSTITUTE OF
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BULLETIN OF AGRICULTURAL AND COMMERCIAL
STATISTICS.

THE December number of the *Bulletin* has just been issued by the International Institute of Agriculture.

Regarding the 1915-16 cereal crops in the Northern Hemisphere, reports are given for France, Great Britain and Ireland, Luxemburg, India, Algeria, and Egypt, where the crops up till now have come on generally under good conditions.

TABLE I.—Parts per Million.

Date.		Rain.	Snow.	Sulphate.	Nitrate.	Nitrite.	Nitrogen in free ammonia.	Nitrogen in alb. ammonia.	Chlorine.
October 12	$\frac{1}{8}$ in.	R		38	—	—	—	—	14'20
15	$\frac{1}{8}$ in.	R		25	0'15	0'00025	0'148	0'219	10'65
16	$\frac{1}{8}$ in.	R		17	0'12	0'00025	0'131	0'181	10'65
November 14	$\frac{1}{8}$ in.	R		28	0'20	0'002	0'258	0'258	21'30
December 1	$\frac{1}{10}$ in.	R		37	0'20	0'002	—	—	14'2
6	$\frac{1}{10}$ in.	R		20	0'10	0'001	0'23	—	7'1
8	$\frac{1}{8}$ in.	R	S	20	0'10	0'0001	0'197	0'197	7'1
12	3 ins.	S	S	12	0'07	0'005	0'147	0'147	7'1
19	1 in.	S	S	22'3	0'0225	0'0005	0'26	0'26	7'1
20	5 ins.	S	S	12'1	0'0225	0'0002	0'131	0'131	12'65
29	8 ins.	S	S	11'1	0'0225	0'0005	0'164	0'19	7'1
January 6	$\frac{1}{8}$ in.	R	S	5'15	0'05	0'002	0'23	0'16	7'1
11	$\frac{1}{4}$ ins.	S	S	12	0'02	0'0002	0'19	0'19	7'1
15	$\frac{1}{8}$ in.	R		24	0'05	0'003	0'19	0'26	10'65
19	3 ins.	S	S	27	0'10	0'002	0'29	0'26	14'2
22	2 ins.	S	S	13	0'05	0'001	0'19	0'16	10'65
28	$\frac{1}{8}$ in.	S	S	17	0'025	0'001	—	—	7'1
31	$\frac{1}{8}$ in.	R	S	29	0'05	0'001	0'16	0'16	10'65
February 2	1 in.	R	S	11	0'05	0'0005	0'296	0'148	7'1
6	1 in.	S	S	12	0'38	0'002	0'23	0'59	7'1
13	$\frac{1}{8}$ in.	R	S	27	0'40	0'003	0'23	0'59	7'1
13	$\frac{1}{4}$ in.	R		16	0'20	0'0015	0'39	0'18	7'1
22	in.	R		8'5	0'20	0'001	0'13	0'39	7'1
23	$\frac{1}{8}$ in.	R		14	0'005	0'008	0'26	0'23	14'2
March 5	6 ins.	S	S	33'6	0'03	0'003	0'47	0'29	7'1
6	4 ins.	S	S	12	0'10	0'001	0'26	0'12	7'1
April 7	$\frac{1}{10}$ in.	R		30'9	0'80	0'0035	—	—	6'39
8	$\frac{1}{8}$ in.	R		28'3	0'80	0'0013	—	—	14'20
11	$\frac{1}{10}$ in.	R		22'3	0'40	0'0072	—	—	10'65
14	$\frac{1}{4}$ in.	R		32'6	0'45	0'001	0'59	0'79	7'1
May 2	$\frac{1}{8}$ in.	R		18'8	0'40	0'002	0'23	0'29	7'1
3	$\frac{1}{8}$ in.	R		13	0'20	0'001	0'44	0'23	7'1
7	$\frac{1}{8}$ in.	R		20'6	0'80	0'004	0'889	0'69	7'1
14	in.	R		13'7	0'20	0'002	0'39	0'23	7'1
20	1 in.	R		16	0'20	0'0005	0'16	0'19	3'5
21	$\frac{1}{10}$ in.	R		13	0'20	0'0005	0'16	0'13	3'5
23	in.	R		10'9	0'30	0'004	0'16	0'18	10'65
23	in.	R		10'9	0'30	0'001	0'03	0'23	7'1
25	in.	R		13'7	0'005	0'0015	0'16	0'13	—
26	in.	R		12'01	0'20	0'001	0'19	0'18	7'1
27	0'35 in.	R		6'8	0'40	0'001	0'11	0'13	7'1
28	$\frac{1}{8}$ in.	R		8'6	0'25	0'0004	0'16	0'16	7'1
29	in.	R		15'4	0'30	0'0005	0'16	0'16	3'5
30	$\frac{1}{10}$ in.	R		1'7	0'60	0'002	—	—	7'1
June 7	$\frac{1}{8}$ in.	R		18'8	0'80	0'0008	0'79	1'19	10'65
7	in.	R		4'1	0'20	0'005	0'29	0'23	7'1
12	in.	R		5'1	0'20	0'001	0'39	0'39	7'1
13	in.	R		6'8	0'20	0'00025	0'26	0'23	3'55
15	in.	R		6'8	0'35	0'0005	0'59	0'29	7'1
18	in.	R		13	0'20	0'0005	0'26	0'19	7'1
19	$\frac{1}{4}$ in.	R		5'1	0'25	0'0005	0'29	0'29	7'1

TABLE II.—Pounds per Acre.

Date.		Rain.	Snow.	Sulphate.	Nitrate.	Nitrite.	Nitrogen in free ammonia.	Nitrogen in alb. ammonia.	Chlorine.
October 12	$\frac{1}{8}$ in.	R		0'431060	—	—	—	—	1'61080
15	$\frac{1}{8}$ in.	R		0'283598	0'01721	0'00003	0'01668	0'01374	1'20610
16	$\frac{1}{8}$ in.	R		0'192829	0'01361	0'00003	0'01486	0'02053	1'20610
November 14	in.	R		0'079408	0'00567	0'00006	0'00691	0'00691	0'60496
December 1	$\frac{1}{10}$ in.	R		0'083941	0'04537	0'04437	—	—	1'61080
6	$\frac{1}{10}$ in.	R		0'025374	0'00227	0'00002	0'00521	—	0'16117
8	$\frac{1}{8}$ in.	R	S	0'009452	0'00047	Trace	0'00083	0'00083	0'03555
12	3 ins.	S	S	0'068061	0'00397	0'00028	0'00834	0'00083	0'04539
19	1 in.	S	S	0'042280	0'00042	0'00001	0'49096	0'49096	0'13462
20	5 ins.	S	S	0'113760	0'00207	0'00002	0'01242	0'01242	1'19922
29	8 ins.	S	S	0'168365	0'00334	0'00008	0'02488	0'01621	1'07693
January 6	$\frac{1}{2}$ in.	R	S	0'004868	0'00047	0'00002	0'00217	0'00151	0'06712
11	$\frac{1}{4}$ ins.	S	S	0'090650	0'00151	0'00015	0'01437	0'01437	0'53694
15	$\frac{1}{8}$ in.	R		0'408370	0'00850	0'00051	0'03233	0'04424	1'81214
19	3 ins.	S	S	0'153139	0'00567	0'00011	0'01744	0'01474	0'80540
22	2 ins.	S	S	0'049155	0'00189	0'00004	0'00718	0'00604	0'40278
28	$\frac{1}{8}$ in.	S	S	0'001607	0'00024	0'00001	—	—	0'06712
31	$\frac{1}{8}$ in.	R	S	0'017960	0'00047	0'00001	0'00151	0'00151	0'10667

TABLE II.—Pounds per Acre (continued).

Date.		Rain.	Snow.	Sulphate.	Nitrate.	Nitrite.	Nitrogen in free ammonia.	Nitrogen in alb. ammonia.	Chlorine.
February 2	1 in.	R	S	0'020856	0'00948	0'00001	0'00561	0'00280	0'13461
6	1 in.		S	0'021752	0'00720	0'00004	0'00436	0'01118	0'13462
13	1 in.	R	S	0'025523	0'00376	0'00003	0'00217	0'00558	0'06701
13	1 in.	R		0'010733	0'00134	0'00006	0'02212	0'01021	0'40263
22	1 in.	R		0'144605	0'02268	0'00011	0'06636	0'02212	0'80540
23	1 in.	R		0'238174	0'00085	0'00136	0'04433	0'03913	2'40576
March 5	6 ins.		S	0'381148	0'00340	0'00034	0'05330	0'03489	0'80540
6	4 ins.		S	0'090750	0'00756	0'00007	0'01966	0'00907	0'53693
April 7	1/10 in.	R		0'070103	0'01825	0'00007	—	—	0'14497
8	1 in.	R		0'080254	0'01869	0'00003	—	—	0'40270
11	1/10 in.	R		0'050594	0'00907	0'00016	—	—	0'24161
14	1 in.	R		0'184959	0'02552	0'00006	0'03346	0'04481	0'40270
May 2	1 in.	R		0'213262	0'04537	0'00023	0'02609	0'03290	0'80540
3	1 in.	R		0'221199	0'03403	0'00017	0'07486	0'03913	1'20809
7	1 in.	R		0'233680	0'09074	0'00045	0'09982	0'07827	0'81140
14	1 in.	R		0'154408	0'02268	0'00023	0'03405	0'00609	0'81140
20	1 in.	R		0'363000	0'04537	0'00011	0'03630	0'02042	0'79306
21	1 in.	R		0'147438	0'02267	0'00006	0'01815	0'01475	0'39702
23	1 in.	R		0'124625	0'03403	0'00045	0'01815	0'02041	1'20810
23	1 in.	R		0'049358	0'01361	0'00005	0'00136	0'01044	3'18813
25	1 in.	R		0'233011	0'00085	0'00026	0'02722	0'02212	—
26	1 in.	R		0'067961	0'01134	0'00006	0'01178	0'01021	0'40269
27	0'35 in.	R		0'053316	0'03296	0'00008	0'00862	0'01019	0'55668
28	1 in.	R		0'077127	0'02835	0'00005	0'01815	0'01815	0'81140
29	1 in.	R		0'174683	0'03403	0'00006	0'01815	0'01815	0'39703
30	1/10 in.	R		0'003857	0'01361	0'00005	—	—	0'16107
June 7	1 in.	R		0'084205	0'00386	Trace	0'03585	5'38962	0'48334
7	1 in.	R		0'046509	0'01168	0'00157	0'03289	0'02609	0'80540
12	1 in.	R		0'057643	0'02268	0'00011	0'04424	0'04424	0'80540
13	1 in.	R		0'077137	0'02268	0'00002	0'03859	0'02609	0'39702
15	1 in.	R		0'030855	0'01589	0'00002	0'02687	0'01318	0'32213
18	1 in.	R		0'147068	0'02268	0'00006	0'03949	0'01237	0'09140
19	1 in.	R		0'028926	0'01427	0'00003	0'01644	0'01644	0'40369
Total				4'913128	0'79303	0'05121	1'54454	6'65371	34'03710

months of November and April, 28 and 28.5 parts per million respectively. Of the various substances determined, the chlorine was the most constant, 7.1 parts per million in thirty determinations.

We considered 12 inches of snow equivalent to 1 of rain, and 226,875 lbs. as the weight of 1 inch of rain upon an acre.

We desire to express our thanks to Dr. N. Knight for helpful suggestions in carrying on this work.

Cornell College, Sept. 28, 1915.

ON THE COMBINATION OF PROTEIN WITH HALOGEN ACIDS.*

By J. H. LONG and MARY HULL.

CERTAIN classes of combinations between protein bodies and halogen acids, and in particular hydrochloric acid, have been studied and frequently described. Before the full recognition of the fact that the proteins may act as basic bodies and hold these acids in salt forms, the distinction between such salts and substitution compounds was not clearly made. Hydriodic acid, for example, forms salts with egg albumin, but it forms also substitution products in which the iodine replaces hydrogen in nucleus groups. In this manner relatively large amounts of iodine may be added, but the products lose the properties of proteins.

In the production of these compounds and in the determination of the proportions in which proteins and halogen acids unite, a number of quite different processes have

been employed. The results vary with the process, and we are still without a satisfactory answer to some phases of the general question. Among the earliest papers describing definite combinations between proteins and acid those of Paal may be referred to (*Ber.*, 1892, xxv., 1202; 1894, xxvii., 1827). Paal produced compounds which he considered as definite salts of peptones, containing from 10 to 15 per cent of HCl. These were made by treatment of egg albumin with diluted acid, and also by digestion of the protein by acid and pepsin. In these cases the salts were separated in comparatively pure form, but in most inquiries on the subject the aim has been to determine the ratio of combination between protein and halogen rather than the isolation of the actual compounds. This has been done usually by finding the amount of acid held by a given weight of protein, when an excess is added and this excess measured by the aid of an appropriate indicator. In this manner, for example, Osborne showed by use of tropæolin, that 1 grm. of certain proteins will bind from 9 to 13 cc. of 0.1 N HCl (*Journ. Am. Chem. Soc.*, 1899, xxi., 477 and 486). With the pure protein edestin, the mean amount was 12.7 cc. or 46.3 mgrms. This is 4.63 per cent of the protein weight. Panormow (*Journ. Russ. Phys. Chem. Ges.*, 1899, xxxi., 556, and 1900, xxxii., 249; through *Fahresb. Fortsch. Thier-Chemie*, 1899, xxix., 8, and 1900, xxx., 6) described definite molecular combinations of albumins with several acids which were obtained by mixing the proteins with dilute acids and precipitating by alcohol. The weights of hydrochloric and other acids combined in this manner appear from the analyses, however, to be rather low. In one case a hydrochloride contained HCl amounting to about 3.2 per cent of the weight of the protein.

By aid of titrations with Guenzburg's reagent, Hoffa found that serum albumin will combine with about 6.3 per cent of its weight of HCl, while the albumoses from egg

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albumin will combine with about 7.7 per cent. These values become greatly increased as the proteins undergo digestion (*Jahresb. Fortsch. Thier-Chemie*, 1900, xxx., 52).

Spiro and Pemsel (*Zeit. Phys. Chem.*, 1898, xxvi., 233) followed a different method to determine the amount of acid which may be combined by proteins. This was based on the fact that the hydrochlorides or other combinations may be salted out, as are the proteins themselves. By adding an excess of 0.2 N or 0.1 N acid to the protein solution, then a sufficient amount of ammonium sulphate solution for precipitation, the uncombined excess of acid may be titrated in the filtrate. Results are given for egg and serum albumins. For the former the amount of HCl combined was about 5 per cent of the protein weight and for the latter about 7 per cent in the mean.

By following the general method of Cohnheim and Krieger results were found by Erb which show a far greater maximum combining power of HCl than is indicated by the work of other observers (*Chem. Centr.*, 1901, ii., 359); Cohnheim, "*Chemie der Eiweisskörper*," 126). These results cannot be reconciled with the values obtained by Spiro and Pemsel, who did not observe any marked increase in the amount of HCl held when the weight mixed with the protein is increased. In the Erb experiments the amount of HCl held by 1 gm. of serum albumin increases from 104 mgrms. to 204 mgrms. when the volume of 0.1 N acid used in solution is quadrupled. However, by use of a method identical in principle v. Rhorer (*Arch. Ges. Phys.*, 1902, xc., 368; see also the discussion by Robertson in *Ergebnisse der Physiologie*, 1910, x., 216, where there is a very full citation of the literature) reached the conclusion that the acid held by the protein does not vary as claimed by Erb. He showed further that the method followed by Erb could not be expected to yield accurate results. This conclusion seems justified by the facts.

We have sought to throw some light on the problem by working in a very simple manner and by methods which at first sight might not be expected to give definite results. Our investigations grew out of some experiments intended to show the extent of combination between the acids and solid or coagulated proteins and the behaviour of these compounds on hydrolysis. (See paper "On the Physiological Activity of Combined Hydrochloric Acid," by J. H. Long, *Journ. Am. Chem. Soc.*, xxxvii., 1333; *CHEMICAL NEWS*, cxii., 52 et seq.). In our experiments we have added known volumes of diluted acids to known weights of proteins and have dried the mixtures at a low temperature or over sulphuric acid, followed by drying over solid alkali. It will be seen that reasonably constant results may be secured this way which have some meaning.

While the titration of the excess of free acid standing over a mixture of acid and protein cannot give a correct measure of the acid which may be held because of the ready dissociation of such compounds with liberation of acid, and because also of the behaviour of available indicators in presence of unaltered protein, still the results in this way have some value for comparison. Some of the results reported by other workers and referred to above were thus secured; for example, those by Osborne cited.

We made mixtures of coagulated egg albumin with 25 cc. of 0.1 N HCl and 25 cc. of water, and treated them as described below. The albumin used was in the form of dried, soluble egg albumin, which was weighed out in multiples of gm. portions, dissolved, and poured into a large excess of boiling distilled water containing a little dilute acetic water. By pouring slowly and stirring constantly it is possible in this way to secure a very fine uniform coagulum. For each gm. of weighed egg powder the protein in the coagulum amounts to 700 mgrms. Methyl orange was finally added to the mixed protein and acid and the free acid determined. The difference between this and the acid added is calculated as acid held. The results are of course below the truth somewhat.

Some of these residual titrations were made at once and some after certain intervals. In some cases the acid solution and protein were mixed by stirring without further agitation. In other experiments the mixtures were actively shaken in flasks and then allowed to stand, while finally in other experiments the protein and acid were well rubbed together in a mortar. Table I. gives the results secured.

The table discloses the fact that even after long standing the combination between acid and protein is incomplete if the mixture is simply stirred. Even after thorough shaking the same is true, but constant results come speedily when the mixture is well rubbed in the mortar. We secure practically the same end result from the solid protein in this manner that others have reported for protein solutions. The egg albumin combines with about 3 per cent of its weight of HCl when heat is not applied, and this represents a somewhat constant value for the combination as measured by indicators. For other proteins the results are not necessarily the same, of course.

TABLE I.

	Coag. from grm. egg.	Wt. of HCl held			
		At once.	After 30 min.	After 60 min.	After 90 min.
Mixture made with- out shaking ..	1	0.0065	0.0112	0.0183	0.0189
	2	0.0102	0.0205	0.0284	0.0339
	3	0.0204	0.0412	0.0500	0.0525
Mixture made by active shaking ..	1	0.0076	0.0175	0.0200	0.0211
	2	0.0193	0.0295	0.0394	0.0423
	3	0.0306	0.0554	0.0605	0.0660
Mixture made by rubbing in mortar	1	0.0206	0.0222	0.0215	0.0219
	2	0.0425	0.0429	0.0419	0.0430
	3	0.0690	0.0700	0.0773	0.0740

By heating the proteins with dilute acid solutions on the water-bath and evaporating slowly to dryness an increase in weight follows, which corresponds to the addition of the acid and not to addition of acid plus water, which would be the case if hydrolysis had taken place. This is illustrated by the following experiments, in which a constant weight of fibrin was mixed with increasing volumes of 0.2 N HCl, evaporated slowly to dryness, and weighed after heating to practically constant weight in the electric oven to 105°. The dry weight of the fibrin alone was 0.677 gm. After weighing the residue was mixed with carbonate and nitrate and fused. In the melt the HCl was determined by the Volhard method.

TABLE II.

	Cc. 0.2 N HCl.	Mg. HCl.	Dry wt.	Inc. wt.	HCl found.
1. ..	20.0	146.0	0.740	0.063	0.0635
2. ..	15.0	109.5	0.743	0.066	0.0642
3. ..	12.5	91.2	0.745	0.068	0.0640
4. ..	10.0	73.0	0.742	0.065	0.0666
5. ..	7.5	54.8	0.730	0.053	0.0519
6. ..	5.0	36.5	0.704	0.027	0.0330
7. ..	2.5	18.3	0.696	0.019	0.0176

The determination of the chlorine is much more accurate than is that of the dry weight. It is somewhat difficult to bring the protein, with or without the acid, to a constant weight, but the results show a satisfactory degree of constancy. In Nos. 1, 2, 3, and 4 it is evident we have added a great excess of acid, and that the excess was expelled without adding water by hydrolysis. An amount of acid below that in No. 5 is insufficient to saturate the protein under these conditions. The mean increase in weight for the first four mixtures is 0.0655, while the mean HCl addition in the same 0.0646. It is evident that we have no water addition here. In similar experiments made with egg albumin the mean increase in weight was 0.0680 and the mean HCl content 0.0704.

With this point established the greater number of experiments were concerned with the extent of the halogen acid

addition rather than with the gross weight increase. The experiments were made essentially in the same manner, using casein, fibrin, and egg albumin.

Casein and HCl.

TABLE III.

In each test 750 mgrms. anhydrous casein employed.
Evaporated over live steam.

No.	Cc. 0.2 N HCl.	Mg. HCl.	Mg. HCl held.	Mean of first four.
1. ..	20.0	146.0	69.5	70.9
2. ..	15.0	109.5	72.4	
3. ..	12.5	91.2	70.3	
4. ..	10.0	73.0	71.4	
5. ..	7.5	54.8	52.0	
6. ..	5.0	36.5	34.9	
7. ..	2.5	18.3	17.2	

TABLE IV.

750 mg. of anhydrous casein plus HCl.

No.	Cc. 0.2 N HCl.	Mg. HCl.	Mg. HCl held.	Mean of first four.
1. ..	20.0	146.0	66.6	67.8
2. ..	15.0	109.5	68.8	
3. ..	12.5	91.2	67.5	
4. ..	10.0	73.0	68.5	
5. ..	7.5	54.8	45.8	
6. ..	5.0	36.5	32.9	
7. ..	2.5	18.3	16.4	

As several experiments suggested that a high temperature might have the effect of causing the addition of too much acid, accompanied by some hydrolysis, the later tests were made by evaporating on a water bath, and slowly. Table IV. shows the results secured by this condition of evaporation.

With the lower temperature the acid held is somewhat less, and amounts to 9.04 per cent of the weight of the casein. It is clear that no excess of acid is added in the cases where an excess of acid was mixed with the casein at the outset. The capacity for combination seems to be a constant in this respect, but apparently varies with the temperature. This result, which is confirmed by many others, seems to disprove completely the view of Erb, referred to above, that the amount of acid taken up by the protein increases with the amount added.

Fibrin and HCl.

The fibrin used for these tests was thoroughly washed until white, mixed with toluene and pressed out as dry as possible, after passing a number of times through the meat chopper. The mass so prepared holds enough toluene to keep some weeks unchanged at a low temperature. It is not necessary to freeze it. The experiments were made, as with the casein, by evaporating slowly on a water bath. Two independent sets of experiments, A and B, are given in Table V.

The results here for the larger acid concentrations are very regular and close to a mean value. They are somewhat higher than the corresponding results for the casein, and show, as we found there, that no increase in the amount of HCl combined follows from increase in amount added to the fibrin.

TABLE V.

2.5 gram. fibrin = 750 mgrms. protein plus HCl.

No.	Cc. 0.2 N HCl.	Mg. HCl.	A. Mg. HCl held.	B. Mg. HCl held.	Mean of first four.
1. ..	20.0	146.0	71.1	70.1	70.8
2. ..	15.0	109.5	70.0	70.3	
3. ..	12.5	91.2	71.1	72.1	
4. ..	10.0	73.0	71.1	70.3	
5. ..	7.5	54.8	50.7	51.5	
6. ..	5.0	36.5	31.9	32.8	
7. ..	2.5	18.3	16.4	17.3	

Egg Albumin and HCl.

We have made at different times a large number of tests as to the rate of combination between the acid and this common protein. The egg used for the purpose was referred to above when another experiment was described. It was part of a large lot of clear dried egg white of Chinese origin which was selected because of its solubility and low colour, and which we have used as a standard preparation for a number of years. In these experiments a known amount was weighed and coagulated, as explained above, and small portions of the coagulum to correspond to 750 mgrms. of anhydrous protein taken for each test. Volumes of 0.2 N HCl were added as in the other tests and the mixtures evaporated slowly to dryness on the water bath. After this the residue was dried at 105° to a constant weight. As the coagulum holds a large amount of water the dry weights taken are not as accurately defined as with the casein or the fibrin.

Two sets of experiments are here given, A and B, Table VI.

TABLE VI.

(1.07 gram. egg = 750 mgrms. protein plus HCl).

No.	Cc. 0.2 N HCl.	Mg. HCl.	A. Mg. HCl held.	B. Mg. HCl held.	Mean of first four.
1. ..	20.0	146.0	80.3	70.3	77.7
2. ..	15.0	109.5	84.0	80.3	
3. ..	12.5	91.2	81.8	83.6	
4. ..	10.0	73.0	70.3	71.2	
5. ..	7.5	54.8	51.5	52.0	
6. ..	5.0	36.5	32.8	35.0	
7. ..	2.5	18.3	17.3	16.0	

The values for the egg combination are not as uniform as were the others, but it is clear that no excess of HCl is held by the higher concentrations. Egg albumin seems to have a higher binding power than has fibrin or casein, the relations, calculated for the gram. basis, being :—

Casein 90.4, or 9.04 per cent.
Fibrin 94.4, or 9.44 per cent.
Egg albumin. . . . 103.6, or 10.36 per cent.

These values are much higher than are those found by means of indicators and undoubtedly have as definite a meaning. Before going into any further discussion concerning them, the results given in corresponding experiments with hydrobromic acid and hydriodic acid will be given.

(To be continued).

PERMANGANATE DETERMINATION OF IRON
IN THE PRESENCE OF FLUORIDES.
THE ANALYSIS OF SILICATES AND
CARBONATES FOR THEIR FERROUS IRON
CONTENT.*

By O. L. BARNEBEY.

THE permanganate titration of ferrous iron in the presence of chlorides has attracted attention for a considerable period of time because of the economic importance of the determination of iron, the ease with which iron ores dissolve in hydrochloric acid, and the rapidity of conducting the permanganate titration. While the titration of iron with permanganate in hydrochloric acid solution has been studied by many investigators (see Barnebey, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 1429), the titration of iron in hydrofluoric acid solution has not received the attention which it merits, especially considering that this titration has been the source of much solicitude to the geologist, petrographer, and chemist for many years. Hydrofluoric acid is the most efficient reagent known at present for the

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decomposition of a silicate. A permanganate solution is one of the most convenient oxidising solutions available for oxidation. However, it is generally recognised that when ferrous iron is titrated with permanganate in hydrofluoric acid solution the end-point is fleeting and the result high or worthless. Consequently, any procedure which increases the accuracy of the titration of ferrous iron with permanganate in fluoride solution has direct application to a very important method of analysis. This study has for its object an improved determination of ferrous iron in fluoride solution and its application to the analysis of silicates and carbonates for their ferrous iron content.

Mitscherlich (*Journ. Prakt. Chem.*, 1860, lxxxi., 108, 116; 1862, lxxiii., 455) proposed to decompose the mineral by heating with strong sulphuric acid in a closed tube for a considerable length of time, thus yielding ferrous sulphate, which was subsequently titrated with permanganate. Hillebrand and Stokes (*Journ. Am. Chem. Soc.*, 1900, xxii., 625; *Zeit. Anorg. Chem.*, 1900, xxv., 326; Stokes, *Bull. U.S. Geol. Survey*, 1901, 186; *Am. Journ. Sci.*, 1901, [4], xii., 414) as well as de Koninck (*Ann. Soc. Geol. Belgique*, 1883, x., 101; *Zeit. Anorg. Chem.*, 1900, xxvi., 123) have shown that this method may give erroneous results in the presence of sulphides which cause the reduction of ferric to ferrous iron, which is later titrated, thus yielding a high percentage. Vogt mentions a similar reducing action of sulphides, Cu_2S being the specific reference (*Zeit. Prakt. Geol.*, 1899, 250).

J. P. Cooke, jun., first used sulphuric and hydrofluoric acids for the decomposition and analysis of silicates for their ferrous iron content (*Am. Journ. Sci.*, 1867, [2], xlv., 347; see also Avery, *CHEMICAL NEWS*, 1869, xix., 270; Wilber and Whittlesey, *Ibid.*, 1870, xxii., 2). The method as proposed by him is in general use to-day. This method, in brief, consists in the decomposition of the silicate with sulphuric and hydrofluoric acids in an atmosphere free from oxygen and titration with permanganate. The air must be excluded to prevent the oxidation of the iron during solution. Cooke passed carbon dioxide through the so-called "Cooke water-bath" with inverted funnel cover to exclude the air, added the acid, heated the water in the bath to boiling, shut off the flow of carbon dioxide, allowing the steam to keep the air away from the sample undergoing attack, waited until the silicate was thoroughly decomposed, then passed cold water through the bath to cool the solution, meanwhile passing carbon dioxide, diluted, and then titrated the ferrous iron with permanganate.

This method has several faults:—(1) Rigid care must be exercised to prevent partial oxidation of the dissolving ferrous iron during the decomposition period; (2) the end-point may be more or less indefinite or fleeting; (3) certain naturally occurring substances must be absent or the results are vitiated.

Pratt (*Am. Journ. Sci.*, 1894, [3], xlviii., 149) has attempted to obviate the first mentioned difficulty by avoiding the use of the water-bath and heating the platinum crucible containing the sulphuric and hydrofluoric acids directly, conducting carbon dioxide into the crucible by means of a platinum tube. By the direct heating process he was able to diminish the time of heating to about ten minutes. However, too great concentration of solution was found detrimental, as the strong hot sulphuric acid had a tendency to oxidise ferrous sulphate. Hillebrand obtained good results by this method ("Analysis of Silicate and Carbonate Rocks," *Bull.* 422, 1910, U.S. Geol. Survey).

Hillebrand (*loc. cit.*) gives an excellent discussion of the detrimental influence of sulphides, vanadium, and organic matter, stating that the titration is "entirely unreliable in the presence of organic matter." This author has also studied the effect of grinding upon the ferrous content of minerals, finding that fine pulverisation decreases the quantity of ferrous iron found, which he attributes to the heat effect.

Gage seeks to improve the titration of the iron by the

addition of calcium phosphate to precipitate the fluorine as calcium fluoride (*Journ. Am. Chem. Soc.*, 1909, xxxi., 381). Fromme adds a large amount of finely-divided silicic acid, thus converting the hydrofluoric acid into fluosilicic acid (*Tschermak's Mineralog. u. Petrogr. Mitteil.*, 1909, xxviii., 329). Dittrich used potassium sulphate with silicic acid to remove influence of the fluorine. ("3. Versammlung in Bad Dürkheim," am 29 März, 1910, II. Teil, S. 92—3; *Ber. Versam. Oberrhein. Geol. Ver.*, ii., 92; *Chem. Abst.*, 1911, v., 846). Dittrich and Leonhard (*Zeit. Anorg. Chem.*, 1912, lxxiv., 21) studied the use of the three previously mentioned reagents, recommending the use of 10 grms. of finely-divided silicic acid and 20 to 25 grms. of potassium sulphate in a volume of 100 cc. which contained also 2 cc. of sulphuric acid. Deussen mentions that manganous sulphate, to a certain degree, does away with the source of error (*Zeit. Anorg. Chem.*, 1905, xlv., 425). However, this use of manganous sulphate has been shown to be not only of no value but of great detriment by several authors (Hillebrand, Gage, Dittrich, and Leonhard, *loc. cit.*). Hillebrand (*loc. cit.*) states that:—

"It is possible to titrate ferrous iron in the presence of sulphuric acid, and as much as 5 to 7 cc. of 40 per cent hydrofluoric acid in a total volume of 200 to 400 cc., almost if not quite as exactly as in sulphuric acid alone, provided the iron solution is diluted with air-free water and the titration made immediately after adding the hydrofluoric acid and with all possible dispatch." He says further, "in the presence of little ferrous iron, up to, say, 2 centigrams, and 5 to 7 cc. of 40 per cent hydrofluoric acid, the colour produced by a drop of permanganate lasts some time, but is very evanescent as the ferrous iron, and consequently the manganese salt formed, increases."

TABLE I.—Sulphuric Acid as Preventive.

1 cc. $\text{KMnO}_4 = 0.009186$ gm. Fe (a).

1 cc. $\text{FeSO}_4 = 0.006151$ gm. Fe (b).

	Normality.		Iron—Grm.			Time 0.10 cc. KMnO_4 lasted. Seconds.
	H_2SO_4 .	HF.	Present.	Found.	Error.	
1.	—	1.0	0.1538	0.1543	+0.0005	10
2.	0.05	1.0	0.1538	0.1543	+0.0005	10
3.	0.10	1.0	0.1538	0.1545	+0.0007	15
4.	0.15	1.0	0.1538	0.1552	+0.0014	25
5.	0.25	1.0	0.1538	0.1543	+0.0005	40
6.	0.50	1.0	0.1538	0.1545	+0.0007	70
7.	0.75	1.0	0.1538	0.1543	+0.0005	120
8.	1.0	1.0	0.1538	0.1543	+0.0005	140
9.	2.0	1.0	0.1538	0.1540	+0.0002	130
10.	4.0	1.0	0.1538	0.1543	+0.0005	120
11.	5.0	1.0	0.1538	0.1543	+0.0005	120
12.	8.0	1.0	0.1538	0.1542	+0.0004	30
13.	12.0	1.0	0.1538	0.1556	+0.0018	3—4
14.	16.0	1.0	0.1538	0.16 +	—	—
15.	1.0	1.5	0.1538	0.1545	+0.0007	30
16.	1.0	2.5	0.1538	0.1550	+0.0012	12
17.	1.0	5.0	0.1538	No end-point	—	—
18.	5.0	5.0	0.1538	No end-point	—	—

(a) The iron value of this and other permanganate solutions used in this investigation is the average value obtained by checking against sodium oxalate, ferrous ammonium sulphate, and electrolytic iron.

(b) Approximately 240 grms. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in water containing 20 cc. of concentrated sulphuric acid (sp. gr. 1.84), and diluted to 8 litres. This solution was titrated with the permanganate at the time of using, and its value computed from the iron value of the permanganate.

In the following is outlined a systematic study of various types of agents which suggested themselves as interesting in regard to their effect on the titration of ferrous iron in the presence of fluorides. The effect of each agent is studied under varying conditions of concentration of that agent. Each series of experiments

TABLE II.—Prevention by Phosphates Insoluble in Water.

1 cc. $\text{KMnO}_4 = 0.005068$ grm. Fe.
1 cc. $\text{FeSO}_4 = 0.005822$ grm. Fe.

	Normality.			Phosphate added.	Iron (grm.).			0.10 cc. KMnO_4 lasted. Seconds.
	H_2SO_4 .	H_3PO_4 .	HF.		Present.	Found.	Error.	
1.	—	—	1.0	$\text{Ca}_3(\text{PO}_4)_2$ (a)	0.1456	0.1343	-0.0113	Fleeting
2.	—	—	1.0	$\text{Ca}_3(\text{PO}_4)_2$ (a)	0.1456	0.1368	-0.0088	"
3.	0.75	—	1.0	$\text{Ca}_3(\text{PO}_4)_2$ (a)	0.1456	0.1456	—	"
4.	—	—	1.0	5 grms. $\text{Ca}_3(\text{PO}_4)_2$	0.1456	0.1389	-0.0067	"
5.	—	—	1.0	10 grms. $\text{Ca}_3(\text{PO}_4)_2$	0.1456	0.1363	-0.0093	"
6.	—	—	1.0	20 grms. $\text{Ca}_3(\text{PO}_4)_2$	0.1456	0.1360	-0.0096	"
7.	—	—	1.0	50 grms. $\text{Ca}_3(\text{PO}_4)_2$	0.1456	0.1302	-0.0154	"
8.	0.60	—	1.0	20 grms. $\text{Ca}_3(\text{PO}_4)_2$	0.1456	0.1457	+0.0001	"
9.	—	0.75	1.0	20 grms. $\text{Ca}_3(\text{PO}_4)_2$	0.1456	0.1409	-0.0047	Fleeting
10.	—	1.5	1.0	20 grms. $\text{Ca}_3(\text{PO}_4)_2$	0.1456	0.1429	-0.0027	"
11.	—	3.0	1.0	20 grms. $\text{Ca}_3(\text{PO}_4)_2$	0.1456	0.1455	-0.0001	"
12.	—	—	1.0	FePO_4 (a)	0.1456	No end-point	—	"
13.	—	—	1.0	FePO_4 (a)	0.1456	No end-point	—	"
14.	—	—	1.0	AlPO_4 (a)	0.1456	0.1461	+0.0005	20
15.	0.50	—	1.0	AlPO_4 (a)	0.1456	0.1470	+0.0014	20
16.	—	—	1.0	$\text{Zn}_3(\text{PO}_4)_2$ (a)	0.1456	0.1464	+0.0008	5
17.	—	—	1.0	$\text{Zn}_3(\text{PO}_4)_2$ (a)	0.1456	0.1470	+0.0014	5
18.	—	—	1.0	$\text{Mg}_3(\text{PO}_4)_2$ (a)	0.1456	0.1368	-0.0088	7
19.	0.50	—	1.0	$\text{Mg}_3(\text{PO}_4)_2$ (a)	0.1456	0.1414	-0.0042	25
20.	0.50	—	1.0	$\text{Mg}_3(\text{PO}_4)_2$ (a)	0.1456	0.1427	-0.0029	30
21.	1.0	—	1.0	$\text{Mg}_3(\text{PO}_4)_2$ (a)	0.1456	0.1449	-0.0007	30
22.	2.0	—	1.0	$\text{Mg}_3(\text{PO}_4)_2$ (a)	0.1456	0.1455	-0.0001	—

(a) Added solid in excess.

contains the results of a number of titrations with permanganate of measured volumes of standard ferrous sulphate in the presence of measured volumes of hydrofluoric acid and the agent being studied. The total volume in each case was 200 cc. preceding titration unless otherwise designated. Usually, after the end-point reading had been taken and recorded, 0.10 cc. of permanganate was added in excess, the solution then stirred, and allowed to stand until the colour bleached out. This procedure was adopted as a test on the stability of the end-point. Ceresin beakers and hard rubber stirring rods were used.

Table I. shows the effect of varying concentrations of sulphuric acid on this titration in presence of fluorides. Experiments 6 to 11 inclusive show that ferrous iron can be titrated at room temperature with moderate accuracy in solutions normal in hydrofluoric acid and normal to 5N sulphuric acid. However, considerably less, or more, sulphuric acid lessens the stability of the end-point.

Titration in phosphoric acid solution of all concentrations between 0.1 N and 0.125 N with normal hydrofluoric acid present gives very fugitive end-points. The use of solutions of the acid phosphates of the alkalis also gives very fleeting and indefinite end-points. Hence phosphoric acid cannot be substituted for sulphuric acid in this titration.

The influence of insoluble phosphates was tried to ascertain if they would give prevention of the indefiniteness of the fluoride end-point. Phosphates of zinc, calcium (Gage, *loc. cit.*), magnesium, iron, and aluminium were used. (See Table II.). Experiments 1, 2, 4, 5, 6, 7, 18, 19, and 20 gave low results because of precipitation of ferrous phosphate, which consequently was not completely oxidised by the permanganate. In 19 the phosphate was added before the sulphuric acid, in 20 the acid before the phosphate, which accounts for a higher result in 20. Experiments 8, 11, and 22 indicate that good results may be obtained when the proper adjustment is obtained between phosphate of calcium or magnesium and acid. However, with calcium phosphate and phosphoric acid the end-points were fleeting, and with magnesium phosphate and sulphuric acid the time test of 0.10 cc. of permanganate was not as favourable as when titrating in sulphuric acid solution without the phosphate (Table I.). The results with calcium phosphate do not confirm the work of Gage. Ferric, aluminium, and zinc phosphates

gave poor results, those with the zinc salt being the best, but the end-point was extremely fleeting. The phosphates tried seem to have little merit as preventives.

The action of alkali bisulphates is similar to the action of sulphuric acid, but the neutral alkali sulphates have but a slight tendency to prevent the fluoride influence.

The influence of a number of bivalent neutral sulphates was tried, among such being zinc, magnesium, calcium, mercury, cadmium, and manganese sulphates. Zinc, cadmium, and mercury sulphates give unstable end-points which lack reliability. Calcium sulphate added as a solid in excess gives end-points which are but slightly more stable. Magnesium sulphate is much more effective. (See Table III.).

TABLE III.—Magnesium Sulphate as Preventive.

1 cc. $\text{KMnO}_4 = 0.009208$ grm. Fe.
1 cc. $\text{FeSO}_4 = 0.006151$ grm. Fe.

Normality.	HF.	50 per cent $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Cc.	Vol. Cc.	Iron (grm.).		
				Present.	Found.	Error.
1.	1.0	10	200	0.1538	0.1532	-0.0006 (a)
2.	1.0	20	200	0.1538	0.1535	-0.0003 (b)
3.	1.0	40	200	0.1538	0.1537	-0.0001 (c)
4.	1.0	80	200	0.1538	0.1539	+0.0001 (d)
5.	1.0	160	200	0.1538	0.1532	-0.0006 (e)
6.	1.8	160	225	0.1538	0.1539	+0.0001 (f)
7.	3.0	180	205	0.1538	0.1535	-0.0003 (g)
8.	3.0	210	335	0.1538	0.1548	+0.0010 (h)

(a) 0.10 cc. KMnO_4 lasts 30 secs.
(b) " " " 40 "
(c) " " " 110 "
(d) " " " 180 "
(e) " " " 20 mins.
(f) " " " 4 "
(g) " " " 90 secs.
(h) " " " 80 "

When the hydrofluoric acid is added to a solution containing magnesium or *vice versa*, a very light precipitate forms. The amount of precipitate increases progressively with the concentration of the acid and magnesium. In Experiment 8 the precipitate was very heavy—probably fluoride of magnesium. The prevention of the fluoride

influence is very marked, surprisingly so in view of the comparatively poor prevention of zinc sulphate.

The detrimental influence of manganese salts is shown in Table IV.

TABLE IV.—Manganese Sulphate as Preventive.

1 cc. KMnO_4 = 0.007866 grm. Fe.

1 cc. FeSO_4 = 0.006151 grm. Fe.

Manganese Solution I. contains 80 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, 150 cc. H_2SO_4 (sp. gr. 1.84), and 150 cc. H_3PO_4 (sp. gr. 1.7) per litre.

Manganese Solution II. = 500 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ per litre.

Normality. HF.	Mn soln. I. Cc.	Mn soln. II. Cc.	Iron (grm.).		
			Present.	Found.	Error.
1. 1.0	1	—	0.1538	0.1544	+0.0006 (b)
2. 1.0	5	—	0.1538	0.1544	+0.0006 (b)
3. 1.0	20	—	0.1538	No end-point	
4. 1.0	—	1	0.1538	0.1663	+0.0125 (c)
5. 1.0	—	10	0.1538	0.17+	
6. 1.0	—	20	0.1538	No end-point	
7. 1.0	—	40	0.1538	No end-point	
8. 1.0	—	10 (a)	0.1538	No end-point	

(a) + 20 cc. of ion H_2SO_4 .

(b) End-point fleeting.

(c) End-point very fleeting.

Manganese salts are thus seen to vitiate results to an enormous extent; when present in any considerable quantity, they absolutely inhibit a good titration.

The effect of a number of trivalent sulphates was tried, and that of ferric sulphate found to be of most interest (Table V.).

TABLE V.—Ferric Sulphate as Preventive.

1 cc. KMnO_4 = 0.009186 grm. Fe.

1 cc. FeSO_4 = 0.006136 grm. Fe.

$\text{Fe}_2(\text{SO}_4)_3$ Solution.—500 grms. crystallised ferric sulphate + 40 cc. H_2SO_4 (sp. gr. 1.84) per litre.

Normality. HF.	$\text{Fe}_2(\text{SO}_4)_3$ Cc.	Iron (grm.).			10 cc. KMnO_4 lasted.
		Present.	Found.	Error.	
1. 1.0	10	0.1534	0.1531	-0.0003	2 minutes
2. 1.0	20	0.1534	0.1529	-0.0005	5 minutes
3. 1.0	40	0.1534	0.1529	-0.0005	14 minutes
4. 1.0	80	0.1534	0.1530	-0.0004	Time not taken
5. 3.0	200	0.1534	0.1516	-0.0018	(Vol. 325 cc.)

Ferric sulphate gives good prevention, but with a large amount of hydrofluoric acid a light pink to lavender colour is imparted to the solution which is somewhat troublesome (Experiments 4 and 5). When ferric sulphate is added to hydrofluoric acid solutions the colour of ferric salts disappears practically entirely until an excess of ferric iron has been added. Aluminium sulphate gave some preventive effect, but it was not sufficiently satisfactory to be of especial merit. A few experiments using bismuth sulphate were performed. While this salt seemed to improve the end-point the improvement was not of sufficient degree to have any value for the purposes of this work. The effect of cerous sulphate was tried and found to be detrimental rather than beneficial.

Cobalt, chromium, nickel, and copper sulphates gave coloured solutions when added to hydrofluoric acid solutions, and thereby prevented the appearance of good end-points.

The effect of a number of oxides was tried to ascertain if they react with the hydrofluoric acid so as to yield undissociated fluorides in solution. Oxides of aluminium, magnesium, and zinc are not applicable, inasmuch as when added in excess they precipitate hydroxide of iron, thus hindering a good clean-cut reaction. Addition of stannic oxide produced apparently no effect, giving a fleeting end-point. The yellow colour of tungstic oxide interfered during titration and the end-point was not stable.

Table VI. gives the tabulated results obtained using molybdic oxide.

TABLE VI.—Molybdic Oxide as Preventive.

(Iron and permanganate solutions the same as used in Series V.).

Normality. HF.	Solid MoO_3 in excess.	Iron (grm.).			10 cc. KMnO_4 lasted, Seconds.
		Present.	Found.	Error.	
1. 1.0	—	0.1534	0.1536b	0.1542b	15
2. 2.0	—	0.1534	0.1509b	0.1547b	6
3. 1.0	—	0.1534	0.1538b	0.1540b	10
4. 1.0	—	0.1534	0.1534b	0.1536b	16
5. 1.0	—	0.0062	0.0073b	0.0073b	(a)
6. 1.0	—	0.0006	0.0010b	0.0010b	(a)
7. 0.05	—	0.0006	0.0010b	0.0010b	(a)
8. 1.0	$(\text{NH}_4)_2\text{MoO}_4$	0.1534	0.1534b	0.1536b	(a)
9. 1.0	solution	0.1534	0.1532b	0.1534b	(a)

(a) Time not taken, but pink end-point was fleeting in each case.

Results designated "b" were obtained by noting the volume of permanganate required to cause disappearance of the blue coloration formed by the reduction of the molybdenum by the ferrous iron. Results designated "p" are those obtained by utilising the volume of permanganate required to tinge the solution pink.

Columbic and tantallic oxides apparently produced no effect because of the slow solution of these oxides in hydrofluoric acid. If freshly precipitated undoubtedly this action would be faster.

Titanium dioxide gives excellent prevention (Table VII.).

TABLE VII.—Titanium Dioxide as Preventive.

(Iron and permanganate solutions the same as used in Series V.).

Normality. HF.	H_2SO_4	Solid TiO_2	Iron (grm.).			10 cc. KMnO_4 lasted. Mins.
			Present.	Found.	Error.	
1. 1.0	—	Excess	0.1534	0.1539	+0.0005	90
2. 2.0	—	Excess	0.1534	0.1534	—	60
3. 5.0	—	Excess	0.1534	0.1533	-0.0001	25
4. 1.0	1.0	Excess	0.1534	0.1534	—	80

(To be continued).

NOTICES OF BOOKS.

The Theory of Valency. By J. NEWTON FRIEND, D.Sc. (Birmingham), Ph.D. (Würz.), F.I.C. Second Edition. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1915.

THE author of this book has some progress to report in the second edition, although no satisfactory theory of valency has yet been advanced. The treatment of the subject is historical, early theories of chemical combination being first briefly discussed, and the clear accounts of the various theories which have been put forward are admirable; in every case the gist of the matter is given without any unessential details, and the student will not only learn the facts, but will also be shown an excellent model of a scientific treatise.

The Positive Sciences of the Ancient Hindus. By BRAJENDRANATH SEAL, M.A., Ph.D. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1915.

THIS book contains discussions with constant references to and quotations from Sanskrit texts, of the knowledge of the Hindus relating to the natural sciences. Some parts of the book have already been published in Dr. P. C. Ray's "Hindu Chemistry." It is difficult to assign exact

dates to the literature which has been chiefly consulted, but for the most part it may be referred to the period 500 B.C. to 500 A.D. The book treats of chemistry, mechanics, acoustics, and biology, and contains much that is of great interest to present day scientific men, though it no doubt requires an expert to estimate its time value. The surprising amount of theoretical knowledge and practical skill which the Hindus of the period had at their command will be a revelation to a good many readers.

The Metallurgy of Gold. By Sir T. K. ROSE, D.Sc. Sixth Edition. London: Charles Griffin and Co., Ltd. 1915.

THE sixth edition of this book has undergone considerable alteration, and much of it has been rewritten, the metallurgy of gold having seen rapid development in the last few years. A good bibliography is included, which, though not giving the title of every article or work on gold which has appeared in scientific literature, omits none which are of importance, and the properties of gold, its alloys and compounds are very exhaustively treated. Detailed accounts of different methods of treating gold ore, with special reference to the underlying principles, are included, and the book is a useful addition to Messrs. Griffin's Metallurgical Series.

A Laboratory Outline of Elementary Chemistry. By ALEXANDER SMITH, B.Sc. (Edin.) British Edition. London: G. Bell and Sons, Ltd. New York: The Century Co. 1915.

THIS companion volume to the author's "Text-Book of Elementary Chemistry" provides an excellent course of laboratory work which the average student will undoubtedly find particularly interesting. Besides the preparation of many elements and compounds, and some simple quantitative experiments, such subjects as the constituents of foods, dyeing, and fermentation are studied in outline, and although the apparatus and methods described are invariably comparatively simple a really wide knowledge of chemical operations and the properties of substances would be obtained by working through the book.

A Text-Book of Elementary Chemistry. By ALEXANDER SMITH, B.Sc. (Edin.), Ph.D. (Munich). British Edition. London: G. Bell and Sons, Ltd. New York: The Century Co. 1915.

THIS text-book has been written specially for the use of students who do not intend to continue the study of the subject, and who require a fairly wide and practical rather than a detailed knowledge. Many allusions are made to the chemistry of every-day life and to substances which have special importance in trade and industry, and the book is of the type which should be used and mastered by every boy, in precisely the same way as he uses his text-book of English history. An abundance of good questions, many of them requiring a certain amount of independent thought and reasoning, is provided, and care is taken to introduce new facts and principles only when the pupils' minds may reasonably be supposed to be ready to digest them. In the British edition two new chapters have been added, on the Laws of Chemical Combination and the Experimental Determination of Equivalent and Atomic Weights, and on the Periodic Classification of the Elements respectively, and some small alterations have been made.

The Chemistry and Technology of Printing Inks. By NORMAN UNDERWOOD and THOMAS V. SULLIVAN. London: Constable and Co., Ltd. 1915.

A BRIEF account of the chemistry and manufacture of printing inks is given in this book, which has evidently been

prepared with care and judgment, though the price at which it is issued is rather high considering the amount of material it contains. The testing of materials used in making printing inks is first treated, the apparatus used, and the methods of analysis employed being described. The manufacture and properties of ink-making materials are the subject of the next chapter, which contains many tables of useful data. The manufacture of printing inks is also treated, and an account is given of some difficulties met with in using typographic inks, and their remedies.

An Experiment in Industrial Research. Board of Education, Educational Pamphlets, No. 30. London: Eyre and Spottiswoode. 1915.

THIS pamphlet contains an account of an attempt made by certain universities in the United States to provide for the necessary co-operation between manufacturers and the universities in the promotion of research. The report was prepared by Mr. T. Ll. Humberstone, and is based upon the observations he made during his visits to the Universities of Kansas and Pittsburgh in 1913, and has been supplemented by later information obtained from America. The scheme described was devised by the late Prof. Robert Kennedy Duncan, and was found to work satisfactorily. It consisted in the establishment of Industrial Fellowships at the University; the selected Fellow undertakes any special piece of investigation desired by a manufacturer, giving a short time per week to teaching in the chemical department of the University. The manufacturer provides the funds for the Fellowship, and in return the Fellow assigns to him the rights relating to any discovery made in the course of the research. A monograph embodying the results of the research is prepared at the expiration of the Fellowship. Some of the details given of the researches carried out under the scheme show that really valuable work has been done, and some of the difficulties of bringing manufacturers and the universities into touch with one another have been successfully solved by it.

The Magnet of Commerce. Second Edition. London: The Great Central Railway Co.

THE first edition of this pamphlet, which was issued rather more than a year ago, was rapidly exhausted, and in view of the great appreciation of the public and Press the Publicity Department of the Great Central Railway Company wisely decided to prepare a second edition. It gives a detailed account of the Midland coalfield and its developments now in progress, and a full discussion of the distribution of coal, with special reference to the new port at Immingham. All the latest available statistics are included, and the booklet is full of valuable information for coalowners and colliery managers and others who are interested in coal and colliery machinery.

Conductivities and Viscosities in Pure and in Mixed Solvents. By HARRY C. JONES and Collaborators. Washington, D.C.: The Carnegie Institution. 1915.

THE researches described in this monograph were all suggested by the solvate theory of solution, and were carried out for the purpose of ascertaining their bearing upon this theory. The various authors have accumulated a great mass of detail, and have been enabled to draw some important conclusions. The subjects investigated include the viscosity of caesium salts in mixed solvents and the dissociating power of formamide, a substance which is particularly interesting, as it is more closely allied to water than any other organic solvent. A full description is given of a series of radiometric measurements of the ionisation constants of indicators, for which a new spectro-scope was constructed, and of a study of the saponification of an ester which was undertaken for the purpose of ascertaining whether there is any difference in the chemical activity of free and combined water. The results show that the latter is more chemically active than the former. The conductivity of certain organic acids in ethyl alcohol

and the constants of some rarer salts in aqueous solutions were investigated, and also the dissociation constants of free and combined water, and the absorption of potassium from aqueous solutions of potassium chloride.

The Institution of Petroleum Technologists: Its Origin, Progress, and Purposes. London: The Institution of Petroleum Technologists, 1915.

THE Institution of Petroleum Technologists was founded in 1913 for the purpose of promoting the scientific and technical education of those who contemplate petroleum technology as a profession, and disseminating knowledge of all branches of the subject. In order that a petroleum business may be run successfully men of very different qualifications must collaborate, and it is hoped that the Institution will furnish opportunities of encouraging intercourse between geologists, chemists, and engineers who are specially interested in the industry. The founders of the Institution and the members of the Committee are men whose names are widely known in the petroleum world, and the rapid growth of its membership shows that its work is likely to be highly appreciated. The pamphlet contains a short account of its foundation, the regulations, and library catalogue, together with a list of members.

The Electrical Trades Directory and Handbook for 1916. Electrician Office, Salisbury Court, Fleet-street, E.C.

IN spite of the greatly increased difficulty in preparing the above directory under the present conditions, the publishers are sparing no pains to make the new issue as complete as possible. Of its value there can be no doubt, for the industrial war is "coming" and must be fought with as much determination as the present conflict of arms, and for the industrial war a thoroughly good electrical trades directory might be regarded as good as an army corps.

OBITUARY.

PROF. HEINRICH DEBUS, F.R.S.

THE death of Prof. Heinrich Debus, at one time Professor of Chemistry at Guy's Hospital and at the Royal Naval College, Greenwich, has recently occurred at Cassel, in Germany. Prof. Debus, who was born in 1824, lived for many years in England and was for some time examiner in Chemistry to the University of London. He was the author of a treatise "Ueber einige Fundamentalsätze der Chemie" and of a biography of Bunsen, who was Professor of Chemistry at the University of Marburg, where Debus received his education. His best known scientific work dealt with the oxidation of ethyl alcohol by means of nitric acid, in the course of which he prepared glyoxal and investigated its properties. He also did some useful work on the products of the combustion of gunpowder. Professor Debus was elected a Fellow of the Royal Society in 1861 and twice served on the Council.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 18, November 2, 1915.

This number contains no chemical matter.

No. 19, November 8, 1915.

Two Series of Complex Derivatives of Bivalent Platinum corresponding to the Co-ordination Index 6.—L. Tschugaeff and W. Lebedinski.—It is

commonly supposed that the complex derivatives of bivalent platinum correspond to the index of co-ordination 4, while those of tetravalent platinum are characterised by the index 6. The authors have, however, obtained derivatives of bivalent platinum belonging to the type $[Pt_6A]X_2$. When the compound $Pt_2CH_3CN.Cl_2$, prepared by Hofmann and Bugge from acetonitrile and potassium chloroplatinite, is cautiously heated, it is transformed into an isomeric compound, which the authors call the β -derivative, to distinguish it from the original α -compound. These two isomers both fix 4 molecules of NH_3 per molecule, giving two α - and β -chlorides corresponding to the same formula of co-ordination $[Pt_2CH_3CN.4NH_3]Cl_2$. They are perfectly colourless, and very soluble in water, the chlorine being completely ionised. The analysis of the chloroplatinites and picrates, and the measurement of their molecular conductivity show that they contain the complex cation, $[Pt_2CH_3CN.4NH_3]^{++}$. The reactions indicate that the α -compound is $\begin{matrix} CH_3CN \\ | \\ CH_3CN \end{matrix} > Pt < \begin{matrix} Cl \\ | \\ Cl \end{matrix}$, and the β -compound is $\begin{matrix} CH_3CN \\ | \\ Cl \end{matrix} > Pt < \begin{matrix} Cl \\ | \\ NCCCH_3 \end{matrix}$.

No. 20, November 15, 1915.

Action of Cupric Liquids on Saccharose. Determination of Invert Sugar accompanied by Saccharose.—Emile Saillard.—Reducing sugars when not accompanied by saccharose can be determined by cupric liquid. The reduction is generally performed at the temperature of boiling water, and alkaline liquid gives the most accurate and rapid results. When saccharose is present the results obtained are too high, for the saccharose is attacked during the reduction, the action being most marked with cupric liquids which contain the most alkali. The author has found that in given conditions the attack is not constant, varying with the proportion of invert sugar, in such a way that when the quantity of invert sugar is increased the action on the saccharose is diminished. It is at a maximum when no invert sugar is present and at a minimum when the amount corresponds to the quantity of cupric liquid employed; otherwise it seems to protect the saccharose. The author has constructed a table by means of which it is possible to determine the reducing sugars in the products of a beet-sugar factory.

Bulletin de la Société Chimique de France.

Vol. xvii.-xviii., No. 17—18, 1915.

Oxidising Effect of Solar Light.—Eyvind Boedtker.—When di-isobutyl was exposed to the action of light and air for fifteen years it was found that it yielded a compound $C_9H_{22}O_5$. It is curious that a compound containing 9 atoms of carbon should thus be obtained from one containing 8, but apparently the first oxidation product is formaldehyde, which then reacts according to the equation $C_8H_{18} + CH_2O + H_2O + O_3 = C_9H_{22}O_5$. The compound behaves like a ketone of a polyvalent alcohol. When isoamyl nitrite is exposed to light tetracarboxylic methane acid is produced.

New Reaction of Isosulphocyanates.—G. Denigès.—To detect isosulphocyanate in a liquid once or twice its volume of mercuric sulphate is added and after filtration the mixture is heated to boiling. If isosulphocyanate is present a crystalline precipitate is formed. By this method it is possible to detect 0.25 grm. of isosulphocyanic acid per litre.

MEETINGS FOR THE WEEK.

WEDNESDAY, 12th.—Royal Society of Arts, 3. (Juvenile Lecture).

"The Science of some Toys," by J. Swinburne.
THURSDAY, 13th.—Royal Society of Arts, 4.30. "The Romance of Indian Surveys," by Col. Sir T. H. Holditch.

THE CHEMICAL NEWS.

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THE QUALITATIVE ANALYSIS OF THE IRON GROUP IN PRESENCE OF PHOSPHATES.

By ROBERT GILMOUR.

(Concluded from p. 257).

Quantitative Experiments with Fe and Ba.

1. 56 mgrms. Fe, 100 mgrms. Ba, 8 cc. 0.5/N $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. 4/N acetic acid, and 8 cc. 2/N $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. A slight excess of FeCl_3 was added, and the mixture boiled and filtered as usual. The Fe in the precipitate was estimated with KI and $\text{Na}_2\text{S}_2\text{O}_3$, and the Ba in the filtrate as BaSO_4 .

N/10 Thiosulphate required = 17.7 cc. = 97 mgrms. Fe.
 BaSO_4 from filtrate = 0.0586 gm. =

= 34 mgrms. Ba.
Ba originally present 100 mgrms.

Consequently 66 mgrms. of Ba have remained with the FePO_4 precipitate.

2. A similar experiment with 40 mgrms. of Ba:—

N/10 Thiosulphate required = 19.4 cc. = 108 mgrms. Fe.
 BaSO_4 from filtrate = 0.0128 gm. =

= 7.5 mgrms. Ba.
Ba originally present = 40.0 mgrms.

32.5 mgrms. of Ba have remained with the FePO_4 .

3. A similar experiment with 140 mgrms. of Ba:—

N/10 Thiosulphate required = 17.6 cc. = 98 mgrms. Fe.
 BaSO_4 from filtrate = 0.1136 gm. =

= 67 mgrms. Ba.
Ba originally present = 140 mgrms.

Therefore 73 mgrms. of Ba have remained with the FePO_4 .

Fe and Sr.

1. 56 mgrms. Fe, 60 mgrms. Sr, 6 cc. 0.5/N $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. 4/N acetic acid, and 8 cc. 2/N $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. Boiled, filtered, and washed the precipitate. The filtrate gave a small precipitate of SrSO_4 with H_2SO_4 and alcohol. The precipitate contained only a trace of Sr.

2. 56 mgrms. Fe, 150 mgrms. Sr, 8 cc. 0.5/N $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. 4/N acetic acid, and 8 cc. 2/N $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. The filtrate gave a considerable amount of SrSO_4 . The precipitate gave a much smaller amount of SrSO_4 (one-third to one-quarter).

The greater part of the Sr evidently remains in solution in contradistinction to Ba.

Fe and Ca.

1. 112 mgrms. Fe, 60 grms. Ca. An exactly similar experiment to the last one. Tested for Ca with H_2SO_4 and 3 vol. of alcohol. In both cases a precipitate of CaSO_4 was obtained, but that from the filtrate was by far the larger of the two.

The results of these experiments show that the phosphate separation as usually carried out is inaccurate in presence of Ba, and the same applies in a lesser degree to the presence of Sr and Ca. Consequently the alkaline earth metals must be removed before the phosphate, or recourse must be had to the alternative method of removing phosphate with tin and nitric acid before commencing the analysis of the iron group.

The proportion of the Ba which remains with the FePO_4 precipitate is too great to be explained by adsorption. Experiments show that in the absence of acetic acid only a very slight loss occurs when FePO_4 or basic ferric acetate is

boiled with a solution containing Ba. The loss in these cases can probably be explained by adsorption, but in an experiment, on the other hand, in which acetic acid and $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ were present, a much larger loss—in fact roughly a 50 per cent loss—was experienced.

The most probable explanation of this would seem to be that in the presence of acetic acid the FePO_4 is hydrolysed to a considerable extent on boiling. The PO_4 ions would then react with the BaCl_2 present, giving $\text{Ba}_3(\text{PO}_4)_2$, while the FeCl_3 formed would, in the presence of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$, be removed from solution as basic acetate. The $\text{Ba}_3(\text{PO}_4)_2$, temporarily formed and soluble in acetic acid, would be precipitated during the boiling as BaHPO_4 , insoluble in acetic acid.

Action of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and Acetic Acid on FeCl_3 .

The procedure in the following series of experiments was in each case as follows:—

The solution of FeCl_3 was treated with a few drops of Na_2CO_3 solution. The small precipitate formed was then just removed by adding HCl drop by drop. Then the $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and acetic acid were added, the solution was diluted to 60 cc., boiled for about one minute, and filtered hot. The filtrate was then tested for Fe with $\text{K}_4\text{Fe}(\text{CN})_6$.

(The sodium acetate solution used was 2/N and the acetate solution 4/N).

Amount of Fe. Mgms.	$\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ Cc.	H $\text{C}_2\text{H}_3\text{O}_2$ Cc.	Fe in filtrate.
140	5	3	Very little
140	10	3	Trace
140	4	2	Very little
56	4	2	Trace
56	4	2	Yellow filtrate
56	+1		"
56	+28		Trace
56	4	1	Yellow filtrate
56	+56	—	Trace
11	4	2	Yellow filtrate
	+2		"
	+2		"
56	4	0.5	Little
56	4	0.3	Very little
56	4	—	Trace
280	16	5	Very little

* Diluted to two volumes.

The significations of the terms in the last column in terms of coloration with $\text{K}_4\text{Fe}(\text{CN})_6$ are as follows:—

Little = Light blue solution with $\text{K}_4\text{Fe}(\text{CN})_6$
Very little = Pale green "
Trace = Very faint green solution, "

(The plus sign attached to figures in the Fe and $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ columns indicates that further quantities of these reagents were added in a particular experiment, followed by boiling).

Examination of the above table shows clearly that if the amount of acetic acid in any particular case is too great to allow of the complete precipitation of the iron, the addition of a further quantity of sodium acetate will not be effectual in completing the precipitation. On the other hand, the addition of more iron, followed by boiling, will result in the removal of practically all the iron from solution.

In general, 4—5 cc. of 2/N $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and 1 cc. of 4/N acetic acid in a volume of 60—70 cc. will ensure the complete removal of iron up to 140 mgrms. at least.

In order to secure some definite information as to the behaviour of Ni, Co, and Mn in presence of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and acetic acid, a further series of experiments was carried out.

Action of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and Acetic Acid on Ni, Co, and Mn in boiling solution.

(The experiments were conducted in exactly the same manner as in the case of Fe).

Amount of Ni. Mgms.	$\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. Cc.	$\text{H}_2\text{C}_2\text{H}_3\text{O}_2$. Cc.	Behaviour of solution on boiling.
60	4	1	Solution remained clear
150	4	1	"
150	4	0.5	Slight turbidity "
150	5	2	Faint green precipitate
150	8	—	Very faint green "

Cobalt.

145 mgrms. Co, 4 cc. $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. Solution remained clear on boiling.

The addition of another 4 cc. of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and further boiling produced a faint turbidity, which cleared up on adding 0.5 cc. of acetic acid.

Manganese.

135 mgrms. Mn, 6 cc. $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. The solution remained perfectly clear on boiling.

Action of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and Acetic Acid on Co, Ni, and Mn in presence of Phosphate.

The procedure in the following experiments was as follows:—

To the solution containing the metal, $(\text{NH}_4)_2\text{HPO}_4$ and a little NH_4OH were added. The precipitated phosphate was then just dissolved in HCl . $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and acetic acid were added, the solution diluted to 60 cc. and boiled.

1. 60 mgrms. Ni, 2 cc. $2/\text{N}$ $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. On boiling the solution became turbid and a small precipitate separated out.

2. 58 mgrms. Co, 2 cc. $2/\text{N}$ $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. On boiling a violet coloured precipitate of cobalt phosphate separated out.

3. 60 mgrms. Ni, 58 mgrms. Co, 3 cc. $2/\text{N}$ $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. On boiling a heavy violet precipitate of cobalt phosphate separated out, which dissolved almost completely on adding 2 cc. $4/\text{N}$ acetic acid.

4. 54 mgrms. Mn, 2 cc. $2/\text{N}$ $(\text{NH}_4)_2\text{HPO}_5$, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. On boiling manganese phosphate was precipitated in large quantity. It did not dissolve completely on adding 5.6 cc. of $4/\text{N}$ acetic acid and boiling.

Action of H_2S on Solutions of Ni, Co, and Mn in presence of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and Acetic Acid.

1. 150 mgrms. Ni, 2 cc. $4/\text{N}$ acetic acid, 4 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$, water 60 cc. Heated to boiling and passed in H_2S gas for two minutes. The filtrate had a green colour. Added 4 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$, heated to boiling, and again passed in H_2S . Precipitation was incomplete. Again added 4 cc. $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$, boiled and passed in H_2S . The filtrate was colourless and free from Ni.

2. 150 mgrms. Ni, 1 cc. $4/\text{N}$ acetic acid, and 4 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. The filtrate was colourless and practically free from Ni.

3. 60 mgrms. Ni, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. Complete precipitation. Filtrate colourless and free from Ni.

4. 6 mgrms. Ni, 1 cc. $4/\text{N}$ acetic, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. Filtrate colourless and free from Ni.

Cobalt.

1. 58 mgrms. Co, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. of $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. The filtrate was colourless after the first filtration and free from Co. When, however, the filtrate was passed through the same filter a second time it was

found to contain some Co, as shown by a light brown coloration on making alkaline with NH_4OH . (This observation holds good in the case of Ni also).

2. 145 mgrms. Co, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. of $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. The precipitation was complete.

Manganese.

1. 135 mgrms. Mn, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. Heated to boiling and passed in H_2S for three minutes. The solution remained clear.

The experiments show that the precipitation of Ni and Co by means of H_2S is complete in a hot solution containing 1 cc. $4/\text{N}$ acetic acid and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. If more than 1 cc. of acetic acid is present, then a proportionately larger amount of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ must be added.

Separation of Fe from Co and Mn in presence of Phosphate.

1. 56 mgrms. Fe, 6 mgrms. Co, 2 cc. $2/\text{N}$ $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. Added a slight excess of FeCl_3 and boiled to remove Fe and phosphate. The filtrate was colourless and free from Fe. On passing H_2S through the hot filtrate no precipitate appeared, but on adding 4 cc. of $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ and again passing H_2S a black precipitate of CoS was obtained in a few minutes.

3. 56 mgrms. Fe, 5 mgrms. Mn, 2 cc. $2/\text{N}$ $(\text{NH}_4)_2\text{HPO}_4$, 1 cc. $4/\text{N}$ acetic acid, and 6 cc. $2/\text{N}$ $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$. After removing Fe and phosphate as usual heated the filtrate to boiling, passed in H_2S , and then made alkaline with NH_4OH . A buff coloured precipitate of MnS was at once obtained.

3. A similar experiment, with 56 mgrms. Fe and 54 mgrms. Mn. MnS was precipitated in quantity on passing H_2S through the filtrate and making alkaline with NH_4OH .

The results show that the basic acetate separation of Fe and phosphate from Co and Mn is quite satisfactory under the given conditions, even when small amounts of the latter are present.

Action of $\text{NaOH} + \text{Na}_2\text{O}_2$ on Nickel Phosphate and Magnesium Phosphate.

Some precipitated nickel phosphate was boiled for some time with NaOH and a little Na_2O_2 , and afterwards filtered off and washed well. On dissolving in dilute HNO_3 and testing with ammonium molybdate, a little phosphate was found to be present.

Magnesium phosphate on similar treatment gave a residue which still contained a little phosphate.

Solubility of Phosphates in $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$.

116 mgrms. Co precipitated as phosphate required 2 cc. $2/\text{N}$ $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ for complete solution.

120 mgrms. Ni required 3.0 cc. $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$.

108 mgrms. Mn " 3.5 cc. "

Solubility of Phosphates in NH_4OH and NaOH .

Phosphate of Zn Easily soluble in NH_4OH and NaOH .

" Ni " " to blue solution.

" Co Soluble in NH_4OH , rather more difficultly than Ni, giving a wine-red solution.

" Cr Insoluble in NH_4OH , easily soluble in NaOH , but reprecipitated on boiling.

" Mn Insoluble in NH_4OH .

*The Complete Examination of a Solution for Metallic Radicles.**Group I.*

Remove Ag, Pb, and Hg(us) with HCl in the usual manner.

Group II.

Remove and separate the metals of the copper and tin group by the method described in a previous paper (*loc. cit.*).

Group III.

The solution, which will probably occupy about 100 cc., is now boiled to remove H_2S , and concentrated to 20–30 cc.

Add 5 cc. of bench H_2SO_4 (4/N), followed by 40–50 cc. of alcohol. Allow to stand for fifteen minutes and then filter, using the pump if necessary.

Precipitate.—Sulphates of Ba, Sr, and Ca. Wash once or twice, transfer to a small beaker, and boil for ten minutes with 20 cc. of strong Na_2CO_3 solution. Filter off and wash the carbonates, dissolve in a few cc. of dilute acetic acid, and analyse according to the method previously described (*loc. cit.*).

(*Note.*—If extreme accuracy is desired, it may be advisable to separate the Sr and Ca by the action of alcohol and ether on the anhydrous nitrates, since the solubility of $SrSO_4$ is considerably increased by the presence of large amounts of Ca salts, and consequently very small amounts of Sr are not precipitated by $CaSO_4$).

Group IV.

Filtrate.—Contains Al, Cr, Zn, Fe, Ni, Co, Mn, Mg, Na, and K. Heat the filtrate on the water-bath until all the alcohol has been removed, and reserve a portion—say one-third—for the examination for Na and K. To the main portion add NaOH until a permanent precipitate is formed, then 2–3 grms. of Na_2O_2 , and heat to boiling for a minute or two. Filter and wash.

Filtrate. F_1 .—Contains $NaAlO_2$, Na_2CrO_4 , and $NaZnO_2$, as well as most of the phosphate, if this is present. (It may of course contain K and Na, but as Na has already been added the solution is not available for examination for the alkalis). To the filtrate add several grms. of solid NH_4Cl and boil. A white flocculent precipitate indicates Al. Filter, wash well, and confirm Al by the $Co(NO_3)_2$ test. The filtrate from the Al contains CrO_4^{2-} and ZnO_2^{2-} . If the solution is yellow Cr is probably present. Acidify a small portion with dilute HNO_3 , add a few cc. of ether and a few drops of H_2O_2 , and shake. A blue etherial layer indicates Cr. If Cr is present acidify the main portion with acetic acid, heat to boiling, and add $BaCl_2$. Filter off the precipitated $BaCrO_4$ and $BaSO_4$, make alkaline with ammonia, and pass in H_2S gas. A white precipitate indicates Zn).

(If Cr is absent the filtrate from the Al is tested for Zn by simply saturating with H_2S).

Precipitate. P_1 .— $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$, $MnO(OH)_2$, $Mg(OH)_2$, and may contain small amounts of the phosphates of these elements. Dissolve the precipitate in a little HCl (using hot strong acid and $KClO_3$ if necessary), evaporate almost to dryness, and dissolve the residue in water. Test a small portion of the solution for Fe with $K_4Fe(CN)_6$, and dilute the main portion to 60 cc. Add Na_2CO_3 solution until a slight permanent precipitate forms; remove this by adding dilute HCl drop by drop, then add 1 cc. of 4/N acetic acid and 6 cc. of 2/N $Na_2C_2H_3O_2$, followed by $FeCl_3$ until the mixture assumes a pale yellow colour. Boil for a minute and filter hot.

Precipitate. P_2 .—Contains $FePO_4$ and basic ferric acetate. Neglect.

Filtrate. F_2 .—Co, Ni, Mn, and Mg as acetates. Heat to boiling and pass H_2S through the hot solution for five minutes. If no precipitate forms add a little more $Na_2C_2H_3O_2$ solution (4–5 cc.), boil and pass in H_2S . Filter and wash, but do not add any of the washings to the filtrate.

Precipitate. P_3 .—NiS and CoS. $[ZnS]$. Dissolve in 2–3 cc. of concentrated HCl, with the addition of a crystal

of $KClO_3$. Evaporate to dryness. Dissolve in 4–5 cc. of water and divide into two portions.

I. Neutralise one portion with NaOH, and add 1–2 cc. of acetic acid and 1–2 cc. of strong KNO_2 solution, and allow to stand. A yellow precipitate of K cobaltinitrite indicates Co.

II. To the second portion add KCN solution (after neutralising with NaOH if necessary) until the precipitate first formed just dissolves, then add 4–5 cc. of 2/N NaOH and a few drops of Br water and boil. A black precipitate of $Ni(OH)_3$ indicates Ni.

(*Note.*—If Zn has not been identified before it will generally be advisable to examine the precipitate of Co and Ni sulphides for it. This may be done as follows:—Dissolve the mixed sulphides in HCl as above, evaporate to get rid of Cl, dissolve in water, and add NaOH in excess and boil. Cool and filter. If the filtrate contains any Zn as Na_2ZnO_2 , saturate with H_2S . A white precipitate of ZnS indicates Zn. The precipitate of $Co(OH)_2$ and $Ni(OH)_2$ is washed, dissolved in HCl, and tested as before for Co and Ni.

Filtrate. F_3 .—Contains Mn and Mg as acetates. Make alkaline with NH_4OH and pass in H_2S . A flesh-coloured precipitate indicates Mn. The filtrate from the Mn contains Mg. Boil to expel H_2S , add NH_4Cl , NH_4OH , and $(NH_4)_2HPO_4$; stir and allow to stand. A white crystalline precipitate of $MgNH_4PO_4$ indicates Mg.

(*Note.*—If the alkaline earth metals have been detected previously it may be advisable to remove traces of these which may be present in solution by adding a few drops of H_2SO_4 to remove Ba and Sr, and a few drops of $NH_4OH + (NH_4)_2C_2O_4$ to remove Ca. The solution is then filtered and tested for Mg with $(NH_4)_2HPO_4$).

The portion of the original solution, after removal of Ba, Sr, and Ca, which was reserved for examination for K and Na, is treated as follows:—

Add NH_4OH , NH_4Cl , and excess of H_2S water, or pass in H_2S gas, heat to boiling, add $(NH_4)_2CO_3$, and filter.

If Mg has been found to be present, add a volume of alcohol to the filtrate and a little more $(NH_4)_2CO_3$, allow to stand for ten minutes, and filter off the $MgCO_3(NH_4)_2CO_3$. The filtrate is then evaporated to dryness, ignited to remove ammonium salts, dissolved in a few cc. of water, and examined for K and Na. If Mg is absent the treatment with alcohol is omitted and the first filtrate evaporated, ignited, and examined for K and Na.

The examination for Na and K may be made in the usual way—i.e., flame tests and formation of potassium cobaltinitrite, or recourse may be had to the method of Mathers and Lee, in which fluoboric and fluosilicic acids are used (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1515).

The following analyses were carried out and proved to be quite satisfactory:—

	Al	Cr	Zn	Fe	Co	Ni	Mn	Mg	Ca	Sr	Ba
I.	56	—	64	56	58	60	54	—	—	—	—
II.	—	—	—	56	—	30	27	—	10	—	12 + Phosphate.
III.	—	—	—	—	58	60	54	24	—	—	—
IV.	28	10	16	28	29	15	14	12	—	—	— + Phosphate.

Chemistry Department,
University of Edinburgh.

Electrical Production of Nitrates.—A course of six lectures on "Electrical Production of Nitrates for Fertilisers and Explosives" will be delivered at the University of London, University College, by E. Kilburn Scott, M.I.E.E., A.M.Inst.C.E., on Wednesdays, at 5.30 p.m., beginning January 26, 1916. The first lecture is open to the public without fee or ticket. The course is open both to members and non-members of the University; fee, £1 11s. 6d. Applications for tickets of admission to be made to WALTER W. SETON, M.A., D.Lit., Secretary, University College, Gower Street, W.C.

ON THE COMBINATION OF PROTEIN WITH
HALOGEN ACIDS.*

By J. H. LONG and MARY HULL.

(Continued from p. 7).

Hydrobromic Acid and Protein.

PORTIONS of the three proteins were treated with 0.2 N HBr exactly in the manner given for HCl. The bromine was found after fusion of the dry residue.

TABLE VII.

750 mg. of anhydrous casein plus HBr.

No.	Cc. 0.2 N HBr.	Mg. HBr.	Mg. HBr held.	Mean of first four.
1. ..	30.0	485.7	273.0	273.9
2. ..	27.5	445.2	274.0	
3. ..	25.0	404.8	275.0	
4. ..	20.0	323.8	273.5	
5. ..	15.0	342.8	227.4	
6. ..	12.5	202.4	193.8	
7. ..	10.0	161.9	153.4	
8. ..	7.5	121.4	116.8	
9. ..	5.0	80.9	79.1	
10. ..	2.5	40.5	39.7	

TABLE VIII.

2.5 grm. fibrin = 750 mgrms. protein plus HBr.

1. ..	30.0	485.7	295.0	291.8
2. ..	27.5	445.2	286.0	
3. ..	25.0	404.8	297.0	
4. ..	20.0	323.8	289.3	
5. ..	15.0	242.8	226.8	
6. ..	12.5	202.4	190.3	
7. ..	10.0	161.9	150.9	
8. ..	7.5	121.4	114.7	
9. ..	5.0	80.9	78.7	
10. ..	2.5	40.5	40.4	

TABLE IX.

1.07 grm. egg albumin powder = 750 mgrms. protein
plus HBr.

			Mean of first three.
1. ..	30.0	485.7	376.5
2. ..	27.5	445.2	378.7
3. ..	25.0	404.8	370.7
4. ..	20.0	323.8	309.2
5. ..	15.0	242.8	224.7
6. ..	12.5	202.4	179.7
7. ..	10.0	161.9	147.8
8. ..	7.5	121.4	109.2
9. ..	5.0	80.9	76.5
10. ..	2.5	40.5	39.6

The above results show that hydrobromic acid is taken up in large quantity by the three proteins and in amounts relatively much greater than is hydrochloric acid. For 1 grm. of the proteins the acid combination is as follows:—

Casein .. 365 mgrms., or 36.5 per cent.
Fibrin .. 398 mgrms., or 38.9 per cent.
Egg albumin 500 mgrms., or 50.0 per cent.

It is evident that the combination cannot be on the same basis as that of the hydrochloric acid, as the amounts combined are not in the proportion of 36.5 to 80.9. But the weights combined with 1 grm. of protein stand in the same order for the two acids, as seen by these figures, the amount held by the casein being called 100.

HCl. Casein ..	100.0
HBr. " ..	100.0
HCl. Fibrin ..	104.4
HBr. " ..	106.6
HCl. Egg albumin ..	114.6
HBr. " ..	137.0

For the casein the HCl and HBr combined are in the proportion of 90.4 mgrms. to 365 mgrms. for the grm. of protein, or nearly in the ratio of 5 to 9 molecules; for the HBr combination with fibrin the ratio is a little higher with reference to the HCl; for the egg albumin the HCl and HBr combinations stand to each approximately in the proportion of 5 to 11 molecules. These numbers probably have some significance, which will be taken up below.

Hydriodic Acid and Protein.

By the same general plan combinations between the three protein bodies and hydriodic acid were made, but a little study showed that the constancy in combining ratios found with the other acids is lacking here. When this acid is added to prepared proteins and the mixture evaporated the increase in weight is roughly in agreement with the iodine taken up, calculated as HI; but sometimes there is a discrepancy, and the total increase in weight may even be less than the added iodine. This can be the case only when something else is driven out of the protein molecule, that is when a substitution as well as an addition follows. This is seen from Tables X. and XI. In the experiments made with egg and fibrin these results were secured.

TABLE X.

1.07 grm. egg albumin powder, equivalent to 750 mgrms
protein and 806 mgrms. dry residue, plus HI.

No	Cc. 0.2 N HI.	Mg. HI.	Dry residue.	Inc. weight.	Mg. HI held.
1. ..	30.0	768	1400	594	588
2. ..	25.0	640	1278	472	463
3. ..	20.0	512	1185	379	381
4. ..	15.0	384	1111	305	287
5. ..	12.5	320	1082	276	245
6. ..	10.0	256	1014	208	197
7. ..	7.5	192	985	179	161
8. ..	5.0	128	919	113	108
9. ..	2.5	64	866	60	53

In four additional experiments with the largest amount of 0.5 N acid added, 30 cc., the weight increase and HI fixed were as follows:—

Increase in weight	603	588	581	572	Mean 586
HI held..	589	561	568	583	Mean 575

It is somewhat difficult to dry these mixtures to constant weight, and this may account for part of the irregularity. In the course of the evaporation and final drying they become dark, which suggests the liberation of iodine, but treatment with carbon disulphide or chloroform fails to bring anything into solution. The results given in Table XI. were secured by repeated experiments with smaller weights of iodine added to the constant weight of egg.

In the first of the above tests in which the 30 cc. of 0.2 N HI was added, the amount held by the protein is over 76 per cent of the weight of the protein. This cannot be accurately titrated by normal alkali, as is the case with the hydrochloric acid combinations of the egg albumin and other proteins. In these combinations the titration results and the chlorine determinations with silver nitrate after fusion agree. It appears, therefore, that the HI combinations by heat are of an order different from those of the HCl compounds, but the combinations made without heat are apparently similar, as will be shown below (Table XII.).

It has been shown in a previous paper by one of us (*Journ. Am. Chem. Soc.*, 1907, xxix, 1334) that HI combines with casein under the same conditions, and to yield compounds containing for 1 grm. of anhydrous casein about 575 mgrms. of iodine, calculated as HI. This ap-

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peared to represent the maximum combining power. Like the other combinations these possessed an ochre colour, suggesting a product resembling the iodabiose of Weyl (*Zeit. Phys. Chem.*, 1910, lxxviii., 236). This product was prepared by adding egg albumin to concentrated hydriodic acid at water-bath heat, and pouring the mixture into an excess of water. The ochre precipitate which formed was purified by solution in alkali and reprecipitation. The iodine is firmly fixed in the product, which seemed to be lacking in some of the characteristic protein reactions. In all our experiments the iodine was used only in the form of dilute HI solution, and in absence of heat no ochre-red colour was developed. The concentration of the dilute acid in evaporation possibly leads to the same or similar compounds.

TABLE XI.

1.07 grm. egg powder = 750 mgrms. protein plus HI.

Cc. 0.2 N HI.	Mg. HI.	Inc. weight.	Mg HI held.
25	640	436	410
25	640	442	478
		439	444
20	512	415	379
20	512	380	400
20	512	390	394
		395	391
15	384	310	295
15	384	299	298
		305	397

TABLE XII.

2.5 grm. fibrin = 750 mgrms. dry protein plus HI.

No.	Cc. 0.2 N HI.	Mg. HI.	Mg. HI held.
1. ..	30.0	768	595
2. ..	25.0	640	409
3. ..	20.0	512	392
4. ..	15.0	384	303
5. ..	12.5	320	253
6. ..	10.0	256	210
7. ..	7.5	192	153
8. ..	5.0	128	102
9. ..	2.5	64	59

Some later experiments on the combination between casein and hydriodic acid, carried out as were those for the other proteins, gave the following results. The amount of iodine held is much larger than in the earlier experiments, but whether by addition or substitution is not clear. The iodine is calculated as HI.

TABLE XIII.

750 mgrms. dry casein plus HI.

No.	Cc. 0.2 N HI.	Mg. HI.	Inc. in wt.	Mg. HI held.
1. ..	30.0	768	601	587
2. ..	25.0	640	400	394
3. ..	20.0	512	393	379
4. ..	15.0	384	329	306
5. ..	12.5	320	299	242
6. ..	10.0	256	229	202
7. ..	7.5	192	141	137
8. ..	5.0	128	112	100

Most of the compounds of iodine and protein described in the literature are substitution products, and are obtained by the action of the halogen, as solid, tincture, or in KI solution. The products contain from about 5 to 15 per cent iodine, but show reactions deviating from those of proteins in some respects. Such compounds have been described by Hofmeister (*Zeit. Phys. Chem.*, 1898, xxiv., 159), Blum (*Ibid.*, 1899, xxviii., 288), Liebrecht (*Ber.*, 1897, xxx., 1824), Hopkins and Pinkus (*Ibid.*, 1898, xxxi., 1312), Kurajeff (*Zeit. Phys. Chem.*, 1898, xxvi., 462),

Pauly and Gundermann (*Ber.*, 1908, xli., 3999, and 1910, xliii., 2243), and others and are not to be confounded with the salts secured by treatment with weak HI. Because of the easy decomposition of the latter, however, and its marked reducing properties, iodine is liberated to be carried into the molecule.

With the hope of throwing further light on the nature of the reaction, we have repeated a number of the above experiments in such a manner as to remove the excess of acids at a low temperature. This was accomplished by adding the 0.2 N acid to the solid protein as before and allowing the mixtures to stand some weeks over sulphuric acid to remove most of the water. The small evaporating dishes holding the residues were then placed in bell jars over powdered sodium hydroxide to absorb acid vapours. In this manner practically all of the acid was removed and most of the water. The mixtures with HCl and HBr evaporated down without much colour, but the HI mixtures became reddish brown as before. A short, final drying in the air oven was necessary to bring to constant weight. Table XIV. shows the final weights and the halogen content of the products.

Only the larger volumes of acid were added in these experiments.

(To be continued).

PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF FLUORIDES. THE ANALYSIS OF SILICATES AND CARBONATES FOR THEIR FERROUS IRON CONTENT.*

By O. L. BARNEBEY.

(Continued from p. 10).

SILICA and silicic acid were used as preventives. The silicic acid was made in the solution by adding sodium silicate to the acid solution containing ferrous iron and hydrofluoric acid (Table VIII.). Experiments 1, 3, and 6 show that moderately good results can be obtained by using silicic acid as preventive. In Experiment 2 too much silicate was added in proportion to the amount of acid present, and some of the ferrous iron was precipitated, hence the low result. Experiments 4 and 5 are included to show the relative values obtained in presence of hydrofluoric acid with sulphuric acid compared with sulphuric acid plus the silicic acid.

TABLE VIII.—Silicic Acid as Preventive.

1 cc. KMnO_4 = 0.007814 grm. Fe.

1 cc. FeSO_4 = 0.006151 grm. Fe.

Na_2SiO_3 —

	Normality.		Iron (grm.).			0.10 cc. lastcd. Second
	HF.	H_2SO_4	Cc. Na_2SiO_3 .	Present.	Found.	Error.
1.	1.0	0.5	10	0.1230	0.1230	—
2.	2.0	1.0	25	0.1230	0.1180	-0.0050
3.	2.0	2.0	20	0.1230	0.1225	-0.0005
4.	2.0	2.0	—	0.1230	0.1250	+0.0020
5.	5.0	2.0	—	0.1230	0.1266	+0.0036
6.	5.0	2.0	25	0.1230	0.1238	+0.0008

(a) Very unstable.

Granulated silica, prepared by various chemical manufacturers, was tried, but it did not work so well. The pink end-point of the permanganate was far less stable, giving a tendency toward high results, perhaps owing to the more insoluble nature of the silica, or to slight impurities in the silica, or to both causes.

When boric acid is added to hydrofluoric acid in solution, meta-fluoric acid, HBF_4 , is formed, which does not dis-

sociate appreciably to yield hydrofluoric acid in the presence of boric acid. This is illustrated by the fact that a dilute solution of the same will not attack glass (see also Moissan, *Traité de Chimie Minérale*, 1904, ii., 166).

Table IX. gives the results of a study of the effect of boric acid in removing the influence of the fluorine when titrating ferrous salts.

TABLE IX.—*Boric Acid as Preventive.*1 cc. KMnO_4 = 0.007866 grm. Fe.1 cc. FeSO_4 = 0.006156 grm. Fe.

	Normality.		H_3BO_3 solid.	Iron (grm.).			10 cc. KMnO_4 lasted. Mins.
	HF.	H_2SO_4 .		Present.	Found.	Error.	
1.	0.50	—	Excess	0.1231	0.1234	-0.0003	40
2.	1.0	—	Excess	0.1231	0.1232	+0.0001	40
3.	2.0	—	Excess	0.1231	0.1232	+0.0001	20
4.	5.0	—	Excess	0.1231	0.1230	-0.0001	10
5.	1.0	0.50	Excess	0.1231	0.1232	+0.0001	15
6.	0.50	—	Excess	0.2462	0.2460	-0.0002	80

The six experiments of Table IX. indicate a very high degree of efficiency for the boric acid. In Experiment 4 considerable heat was evolved when the boric acid was added. The amount of solid added in each case depended upon the consumption of the boric acid by the hydrofluoric acid. This is easily regulated, since an excess of reagent does no harm. In fact, the excess seems to facilitate obtaining the end-point.

Borax was also tried, adding the solid in excess to the sulphate solution containing HF. Its use produced good end-points, but not as excellent as with boric acid. A saturated solution of borax was also used with success. Inasmuch as the use of boric acid affords such good titrations a point of interest arises at once in regard to how much effect it will have in offsetting the detrimental influence of manganese salts. This is of especial importance, inasmuch as manganese salts have such a good preventive action when titrating ferrous iron in the presence of chlorides and bromides (Table X.).

TABLE X.—*Boric Acid Prevention of the Manganese Effect.*

(Solutions of iron and permanganate the same as in Series IV.).

Boric acid added solid in excess.

	Normality.		Mn solution		Iron (grm.).		0.10 cc. KMnO_4 lasted. Seconds.
	HF.	HCl.	I.	II.	Present.	Found.	
1.	1.0	—	1	—	0.1538	0.1538	(a)
2.	1.0	—	5	—	0.1538	0.1533	(a)
3.	1.0	—	20	—	0.1538	0.1539	(a)
4.	1.0	0.03	20	—	0.1538	0.1536	60
5.	1.0	0.15	20	—	0.1538	0.1538	40
6.	1.0	0.30	20	—	0.1538	0.1538	35
7.	1.0	0.60	20	—	0.1538	0.1542	20
8.	1.0	0.90	20	—	0.1538	0.1536	12
9.	1.0	0.90	30	—	0.1538	0.1538	20
10.	1.0	1.5	50	—	0.1538	0.1551	20
11.	—	0.60	—	—	0.1538	0.1571	(b)
12.	1.0	—	—	10	0.1538	0.1533	40
13.	1.0	—	—	40	0.1538	0.1543	5
14.	1.0	0.60	—	10	0.1538	0.1539	4
15.	1.0	—	—	—	0.1538	0.1538	120

(a) Definite; time not noted.

(b) Not definite.

In the experiments of Table X. the time listed for disappearance of the pink colour of the permanganate is only for the disappearance of the deep pink; a lighter shade of pink remained (except in Experiments 11, 13, 14) for a longer period of time than that designated. In Experiment 11 the odour of liberated chlorine was strong. In Experiment 15 after the 0.10 cc. of KMnO_4 added in excess had bleached, 0.10 cc. more of KMnO_4 was added, and this

addition required eighteen minutes to bleach, after which 0.10 cc. more of KMnO_4 retained its pink colour for over three hours. This series of experiments shows that the fluorine influence can be removed in the presence of manganous salts very effectively. Hence in the presence of fluorides, bromides, and chlorides the addition of a manganous salt and boric acid allows ferrous iron to be titrated accurately with permanganate.

Inasmuch as hydrofluoric acid solutions of ferrous iron are readily oxidised by the air it was decided to study the stability of fluoboric acid solutions of ferrous iron. To measured portions of standard ferrous sulphate were added measured volumes of 10 N HF; the solutions were diluted to a definite volume, and allowed to stand varying lengths of time, after which boric acid was added in excess and the ferrous iron titrated. These results were compared with those obtained by adding an excess of boric acid to the fluoride solution immediately after adding the hydrofluoric acid and allowing to stand an equal time.

TABLE XI.—*Stability of Fluoboric Acid Solutions of Ferrous Iron.*1 cc. FeSO_4 = 0.006113 grm. Fe.1 cc. KMnO_4 = 0.009184 grm. Fe.

	Normality. HF.	Volume.	Time.	Iron (grm.).	
				Present.	Found.
1.	1.33	150	10	0.0611	0.0551 (a)
2.	1.33	150	20	0.0611	0.0543 (a)
3.	1.33	150	40	0.0611	0.0518 (a)
4.	1.33	150	30	0.1223	0.1139 (a)
5.	1.33	150	30	0.3057	0.2948 (a)
6.	1.33	150	10	0.0611	0.0613 (b)
7.	1.33	150	20	0.0611	0.0611 (b)
8.	1.33	150	40	0.0611	0.0613 (b)
9.	1.33	150	30	0.1223	0.1223 (b)
10.	1.33	150	30	0.3057	0.3053 (b)
11.	1.33	100	60	0.1834	0.0743 (c)
12.	1.33	100	60	0.1834	0.1834 (d)

(a) Solid boric acid added after standing.

(b) Solid boric acid added in excess before standing.

(c) No boric acid added. Aerated.

(d) Solid boric acid added in excess. Aerated.

The results confirm the observations of others regarding the ease of oxidation of ferrous salts in the presence of hydrofluoric acid. However, the addition of boric acid makes the solution so much more stable that the oxidation is negligible in a moderate length of time. In Experiments 11 and 12 air was bubbled through the solutions at the rate of about three bubbles a second for an hour. A cersin bottle was used to hold the solutions and the glass tubes used for conducting the air in and out of the vessel were coated with paraffin. In this case more thorough agitation was accomplished, and the solution was kept more nearly saturated with air. Even in this case the theoretical result was obtained when boric acid was added before agitating. However, without the addition of boric acid about 57 per cent of the ferrous iron was oxidised by the air.

Boric acid is the best of all the agents studied, since it removes the fluorine influence in the iron titration so effectually, is so easily prepared in a high degree of purity, is inexpensive, and is sparingly soluble in water, so that the addition of the solid can be easily regulated according to the amount of hydrofluoric acid present. A number of silicate analyses have been made, and the following method has been found applicable (Table XII.).

Analysis of Silicate and Carbonate Rocks.

An appropriate sample (0.5 to 5 grms.) in a capacious platinum dish is covered with water, and placed on a Cooke water-bath (*loc. cit.*) in which the water has been previously thoroughly boiled to remove dissolved oxygen. Carbon dioxide is passed for several minutes, or steam allowed to escape for several minutes, or both, to

remove any air inside of the glass funnel, after which 5 cc. of 1:1 H_2SO_4 (HCl can be used) is added by pouring down the platinum stirring rod. If carbonates are present care must be exercised to prevent too violent action. Should soluble sulphides be present the acid is likewise added slowly to expel the H_2S as completely as possible. Strong hydrofluoric acid is then added, 5 cc. to 20 cc. depending upon the size of the sample, pouring down the stirring rod. The bath is maintained at an even temperature, a continuous current of steam being expelled through the funnel until the silicate is thoroughly decomposed. If carbon dioxide is allowed to pass through the bath continuously it should be regulated so that its passage is slow, just sufficient to give direction to the current of escaping gases. Occasionally a little previously boiled water is added to the bath to maintain the water level. For this purpose a flask of boiling water should be kept constantly ready for use.

When decomposition is complete the funnel is lifted from its place, and cold (previously boiled) distilled water added immediately to the dish to dilute the solution somewhat, followed immediately by an excess of solid boric acid. The solution is stirred, then lifted from the bath. If solid organic matter is present it should be filtered through an asbestos filter using suction (a carbon funnel with a Witte plate is convenient for this purpose), and the filter washed with previously boiled distilled water. The solution is poured into a glass beaker, diluted to a convenient volume, and titrated with standard permanganate. If the solution has been filtered it is titrated in the suction flask. It is well to add some solid boric acid before titrating to give the same colour effect as usual at the end-point. When hydrochloric acid is used for the decomposition of the sample, some substance should be added to counteract its influence when the ferrous iron is titrated. Since the hydrofluoric acid has been transposed to fluoboric acid any good preventive is applicable (Cooke, *loc. cit.*). Ten to 20 cc. of the ordinary preventive solution (Barnebey) used in the iron titration—80 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ + 80 cc. H_2SO_4 (sp. gr. 1.84) + 80 cc. H_3PO_4 (sp. gr. 1.7)—per litre is effective, or the phosphoric acid may be omitted, and 160 cc. of sulphuric acid used in preparing this solution.

The above method can be easily adapted to Pratt's scheme of decomposing the silicate, which requires less time because of the application of a higher temperature. The sample is placed in a platinum crucible, carbon dioxide is conducted into the crucible by means of a platinum tube, which is inserted under one edge of the cover, acid is added, and heat applied directly to the crucible. As soon as steam is evolved copiously the carbon dioxide is shut off, hydrochloric acid added, and the cover fitted snugly to the crucible. When decomposition is complete dilute somewhat with water, add boric acid and proceed as usual.

(To be continued).

FIXATION OF ATMOSPHERIC NITROGEN.*

By LELAND L. SUMMERS.

Introductory.

IN 1898 Sir William Crookes in his Address as President of the British Association very forcibly pointed out that the commercial fixation of atmospheric nitrogen was one of the greatest discoveries awaiting the ingenuity of chemists. He emphasised with very interesting figures its important practical bearing on the future welfare and happiness of the civilised races. This Address brought forcibly to the attention of engineers the fact that the existing sources of fixed nitrogen were limited, and greatly

stimulated the efforts of investigators. The problem itself had been worked on for over a century, as it was known that nature fixed nitrogen of the atmosphere by means of electric discharges, and Cavendish in 1781 had shown that a small amount of nitrogen was converted into nitric acid in the combustion of hydrogen with oxygen to form water, while Bunsen in 1877 obtained favourable yields by means of gaseous explosions. The earlier efforts commercially in the art were, however, largely confined to the fixation of nitrogen for the purpose of manufacturing cyanides, and the earlier bibliography of the subject therefore deals almost entirely with these efforts.

Commercial Products of Nitrogen.—The three fundamental commercial products formed by nitrogen are: first, its union with oxygen to form nitrates, XNO_3 , and nitrites, XNO_2 ; second, its union with carbon to form cyanogen C_2N_2 and producing cyanides XCN and cyanamids XC_2N_2 ; third, its union with hydrogen to form ammonia, NH_3 . From all of the above products there are obtained a large number of derivatives used in the chemical arts.

The most important of all commercial products are the unions of nitrogen with oxygen, forming the nitric acid salts of commerce. These are of particular importance on account of the vast natural deposits of nitrate of sodium occurring in Peru and Chile, commonly called Chile saltpetre. Practically, this commodity is the one that sets the price for all other compounds of nitrogen, as it has been mined in Chile since 1830, and during the past twenty-five years its production has assumed vast proportions, the present annual output amounting to about 2,500,000 tons. This deposit of Chile appeared inexhaustible, and therefore there was no occasion for alarm regarding the world's supply of combined nitrogen; but after years spent in exploration work it began to appear that the Chilean deposits would be exhausted before the end of the present century, and since then all other sources of combined nitrogen have received attention.

While there are a few scattered natural deposits other than those in Chile, there is none which has at the present time a chance of competing, most of them being of limited extent and situated in inaccessible regions. In Chile the deposits are easily worked, and even after years of careless mining, with no effort to effect economies, the present cost of producing nitrate is not excessive, varying from 10 dols. to 20 dols. per ton and selling in Liverpool for about 45 dols. per ton. This leaves a profit of from 5 dols. to 10 dols. a ton on the operation, after paying the Government of Chile an export tax of about 12.25 dols. per ton. In the past thirty years this export tax has netted the Chilean Government about 500,000,000 dols. Of the total production of Chile the United States imports about 600,000 to 700,000 tons per annum, the balance being practically all shipped to European countries. Chile saltpetre has sold as high as 60 dols. a ton, but since 1909, when the agreement among the producers expired, the price has approximated 45 dols. per ton f.o.b. Liverpool, making a price of from 35 dols. to 40 dols. per ton f.o.b. Chile.

The union of nitrogen and carbon to form cyanides and with hydrogen to form ammonia are two of the earliest forms in which the combined nitrogen was utilised. Most all animal and vegetable refuse contains ammonia compounds, and these were the early sources of ammonia, and animal refuse products such as hides, hoofs, and horns were the sources of combined carbon products forming the cyanides. Until the discovery of the McArthur-Forrest process for gold extraction, the markets for cyanides were comparatively limited and there was no great effort made to produce them on a large scale. With the rapid development of this art in the recovery of the low-grade gold deposits, a sudden impetus was given to the cyanide industry, and large quantities of cyanides are now manufactured from ammonia and metallic sodium. Small amounts of cyanides for industrial purposes are recovered from the gas retort houses, but these processes are not generally applied, and no particular effort has been made to extend the processes

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to the recovery of cyanides from by-product coke ovens. The greater portion of the cyanides are manufactured in England and Germany, and some 20,000 tons per annum are exported annually by these two countries. As the cyanides of sodium and potassium for gold recovery purposes sell from 300 dols. to 400 dols. per ton, they represent one of the highest prices of nitrogen directly combined with a simple element.

The third great commodity of commerce, ammonia, is utilised extensively in industrial arts, but in addition has been used for many years as a fertiliser. The annual production of sulphate of ammonia now amounts to about 1,250,000 tons, and the Liverpool price approximates that of sodium nitrate, varying from 45 dols. to 60 dols. per ton. Practically all of this sulphate of ammonia is manufactured from coal distillation either from gas house retorts or by-product coke ovens, up to the past year there having been practically no process in operation for the direct synthesis of ammonia from its compounds.

All the older retort processes for the manufacture of gas recover ammonia by washing the illuminating gas with water. All by-product coke ovens likewise treat the by-product gas for the recovery of ammonia. American coals run from 0.9 per cent to 1.4 per cent nitrogen, or from 18 to 28 lbs. (8.1 to 12.7 kilogram.) of nitrogen per ton of coal. In the distillation of this coal, about 20 per cent of the nitrogen is recovered from the gases of distillation, so that from $4\frac{1}{2}$ to 7 lbs. (2.1 to 3.2 kilogram.) of ammonia are recovered per ton of coal distilled; this ammonia when united with sulphuric acid forms sulphate of ammonia, giving a yield from 18 to 28 lbs. (8.1 to 12.7 kilogram.) of sulphate of ammonia per ton of coal distilled. Weak solutions of ammonia water are concentrated from the gas-house retorts and the ammonia distilled from this water by breaking down the ammonia contents with lime, the pure ammonia being then united with sulphuric acid. In many of the coke oven plants the sulphate is formed directly by passing the gases into sulphuric acid, forming the ammonia sulphate by a direct process.

In general it costs about 15 dols. per ton of ammonia sulphate to manufacture the sulphate from the ammonia, so that if ammonia sulphate is selling for 45 dols. per ton, 15 dols. of this is represented in the cost of sulphuric acid and the manufacturing, making the net ammonia cost, with profit, 30 dols. per ton of sulphate, or, as the nitrogen content of the sulphate amounts to 21 per cent the nitrogen represents an actual value of 7 cents per lb. With the great increase in the number of by-product coke ovens, there has been a greatly increased quantity of ammonia sulphate manufactured, and it would seem that under these conditions the price of ammonia sulphate will tend to diminish rather than to increase. The actual cost to the by-product coke oven plants recovering the ammonia, in addition to the 15 dols. for manufacturing the sulphate of ammonia, will approximate 10 dols. per ton, and if there is any profit to be obtained from the sale of ammonia, they can afford to recover it at this figure.

Another source of ammonia by coal distillation is from producer gas generated on what is known as the Mond system. In this process steam is admitted to the producer in excess, so that the temperature is not permitted to rise to a point where the ammonia liberated by the fuel is decomposed. This excess of steam tends to protect the ammonia, and it is recovered from the producer gas by washing. In this process not only the ammonia carried in the volatile products is recovered, but also a large percentage which ordinarily remains in the carbonaceous residue of the coke oven and gas-house retort. As ordinarily distilled, about 50 per cent of the total ammonia of the coal remains in the coke residue and is not recovered. In the producer, where this coke is consumed in the presence of steam, the total percentage of recovery may be as high as 75 per cent of the theoretical nitrogen contained in the coal, so that from 15 to 20 lbs. (6.8 to 9.1 kilogram.) of nitrogen may be recovered, or, in terms of ammonia sulphate, from 60 to 80 lbs. (27.2 to 36.2 kilogram.) of

ammonia sulphate may be obtained per ton of coal consumed in the producer. This type of producer has not been extensively utilised in America, as the expense of installation is increased by the necessity of washing a very large volume of low-grade gas, the volume of gas per ton of coal consumed in the producer being about 130,000 cubic feet against about 10,000 cubic feet per ton of coal, as distilled in the coke oven.

A number of these plants have been installed in England and on the Continent, but the aggregate of the ammonia sulphate produced is not large as compared to that from coke ovens and gas-house retorts.

Available Nitrogen in Commercial Products.—The question of the available nitrogen in the various compounds has, in a measure, determined the price of the product, the utilisation in the fertiliser art being practically the basis of fixing the price. For a number of years it has been assumed that the selling price of combined nitrogen would be from 12 cents to 13 cents a lb. Thus Chile salt-petre being about 95 per cent pure, nitrate of soda would have a theoretical nitrogen content of about 16.5 per cent, or, corrected for impurities, would have about 15.5 per cent nitrogen.

As the cyanides, until recently, were not used directly in the fertiliser art, and were combined with more expensive products, their price has not been regulated by their content of combined nitrogen. The ammonia used in the fertiliser art is almost entirely used as sulphate of ammonia, on account of the cheapness of the commercial sulphuric acid and the ease of manufacture, and this product would therefore have a theoretical content of 21 per cent of nitrogen.

The above nitrogen products may be considered the fundamental commercial forms in which combined nitrogen enters the market, and while the fertiliser industry fixes the price of combined nitrogen, it is only one of the many industries in which vast quantities of nitrogen are utilised. Thus about 50 per cent of all the Chile salt-petre imported in this country is used in the manufacture of explosives, while an additional 25 per cent is utilised in the arts requiring nitric acid. Of the ammonia sulphate, a very large percentage is used directly as fertiliser, though there is a very considerable demand for use in chemical industries and such commercial applications as anhydrous and aqueous ammonia used in the refrigeration art. Practically all explosives have utilised nitrogen compounds as a principal ingredient. The earlier makers of black gunpowder used Chile salt-petre, charcoal, and sulphur, and the later so-called smokeless powder utilises the oxygen-carrying property of nitrogen as well as the inherent molecular energy in the production of such high explosives as nitro-glycerin, cordite, lyddite, melinite, gun-cotton, and various other nitro-cellulose compounds, and modified explosives used in industrial work, such as dynamite and various blasting powders.

Fixation Processes.—In considering the fixation of atmospheric nitrogen from a commercial standpoint, the limitations will be imposed by the selling price of the natural product from Chile, covering nitrate compounds, and the selling price of ammonia sulphate, as obtained from coal distillation, affected as these prices will be by the manufacture of ammonia from atmospheric nitrogen.

In competition with the above sources of nitrogen there has been the constant effort toward the fixation or rather the utilisation of some of the vast quantity of atmospheric nitrogen surrounding us.

A list of these fixation processes would contain the names of hundreds of investigators, and from the past twenty years of effort there may develop processes which at present are still experimental; but of the various processes which have reached the state of commercial application there appear to be four distinct lines of development.

First.—The production of nitric acid directly from the atmosphere by means of the electric arc. In this process

the nitrogen of the atmosphere is directly combined with its accompanying oxygen without utilising any other chemical substances, the process consisting essentially of a powerful arc furnace through which air is forced, causing at this high temperature the nitrogen to combine with the oxygen, forming nitric oxide, NO.

Second.—Methods of fixing nitrogen by means of electric furnaces or combustion where the energy of chemical combination is utilised, causing the nitrogen to combine with some substance with which there is a pronounced energy of chemical combination. These processes include furnaces utilising calcium carbide, with which nitrogen readily combines to form calcium cyanamid, CaCN_2 , and various processes for making combinations of nitrogen and a basic or alkaline earth metal such as calcium nitride Ca_3N_2 , or magnesium nitride Mg_3N_2 , or aluminium nitride AlN , the chemical action usually forming a nitride or carbo-nitride.

Third.—Processes for producing ammonia, NH_3 , directly from nitrogen and hydrogen. These include the effort to use the various forms of electric discharge by which the nitrogen molecule may be decomposed and, in the presence of hydrogen, form ammonia. As ammonia decomposes at a very low temperature (500 to 1000° C.) only the silent discharge seems available, and the yields are not commercial. The most promising of all direct ammonia processes seems to be that of Haber. In this process a catalytic agent is used, and under a heavy pressure the nitrogen molecule is decomposed and united to the hydrogen, thus forming ammonia. Salts of uranium seem to be preferred as the catalytic agent, and have the power of acting on nitrogen at a temperature of about 500° C.

Fourth.—Production of a high temperature by combustion, utilising either catalytic agents or simply by producing a high temperature by means of the explosion or combustion of gases directly combining the nitrogen and oxygen to form nitric oxide, NO. This method, early used by Bunsen in the combustion of hydrogen to form water, has been applied to coke oven gases by Hausser. A bomb is used and the mixture of gas and air is fired electrically, the small amount of NO formed is recovered and converted into nitric acid, HNO_3 .

The chemical form in which the commercial supplies of combined nitrogen appear on the market is due largely to existing commercial conditions. The nitric acid combined as sodium nitrate occurs in this form simply on account of being naturally produced in this form. The ammonia appears on the market as ammonia sulphate largely on account of the cheapness with which sulphuric acid can be obtained, and the widely distributed plants for its manufacture, making it one of the cheapest and most convenient forms of combining with ammonia. It is probable that in commercial nitrogen fixing plants, if both ammonia and nitric acid are manufactured, one of the most convenient forms of marketing this product will be by using nitric acid in place of sulphuric acid, making ammonia nitrate, NO_3NH_4 . This product is on the market at present, but is only manufactured from sodium nitrate and from ammonia, or in some of the plants where nitric acid is manufactured, ammonia is shipped to the nitric acid plants to be manufactured into ammonia nitrate. The advantage of ammonia nitrate is that it has a nitrogen content of 35 per cent, in this respect being a much more concentrated nitrogen product either for the processes of manufacturing other compounds of nitrogen or for use in the fertiliser industry.

Physical Limitations and Those Fixed by Natural Sources.—The competition with natural sources will fix the commercial limitations or selling prices for these various nitrogen compounds, and in considering the possible developments of the processes it will be interesting to see to what extent they have definite theoretical limitations, as these will greatly affect any comparison of possibilities. Before considering in detail these processes we might endeavour to investigate whether our present con-

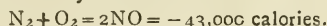
ception of the physical and chemical reactions involved impose real limitations, or whether there is an uncertain boundary which further developments may encroach upon, perhaps thus continually improving the efficiency and possibilities commercially. If, for instance, the nitric oxide processes which utilise only 2 per cent to 4 per cent of the energy supplied to the furnace are limited to this amount by the inefficiency of the apparatus, there are much greater possibilities of development than would be the case if the process has definite physical or thermo-dynamic limitations, and the present apparatus utilises a favourable percentage of this possible ultimate limit. To some extent these theoretical limitations are not always sharply defined, and research will extend this horizon, but we may determine some of these limitations quite definitely.

II. Theoretical Limitations.

As we are considering this subject from its engineering aspects, it may be excusable to examine some of the theoretical limitations imposed by the laws of physical chemistry, and in reviewing what may be termed elementary formula it is interesting to note that the investigation of these theoretical limitations has been of fundamental importance to physical chemistry in extending the application of the laws of chemical dynamics.

Molecular Inertness of Nitrogen.

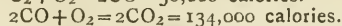
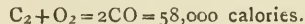
The elements carbon (C) and nitrogen (N) possess a marked similarity in the fact that the molecule of each is composed of two or more atoms united together with a bond representing a large amount of energy. Nitrogen, having an atomic weight of 14, has a normal molecular weight of 28, indicating two atoms to the molecule, and in this molecular form it occupies 79.2 per cent of the volume of the earth's atmosphere. To separate this molecule into its constituent atoms and cause these atoms to combine with other elements is the problem of the fixation of nitrogen. Unless combined in the atomic form the enormous bond between the atoms causes them to combine upon themselves into the inert form of molecular or atmospheric nitrogen. The ordinary compounds of nitrogen are formed only by expenditure of a large amount of energy, the union of molecular nitrogen, N_2 , and molecular oxygen, O_2 , to form nitric oxide, NO, being represented by the formula—



Or in other words, to form 1 grm. molecule of nitric oxide, NO, requires the expenditure of energy amounting to 21,500 calories.

The general similarity to carbon in this molecular inertness makes an interesting comparison.

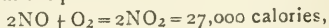
Thus—



The formation of 1 grm. molecule of CO therefore represents the liberation of 29,000 calories, while the formation of 1 grm. molecule of CO_2 and CO represents 67,000 calories, or a total of 96,000 calories in the formation of CO_2 from the original elements C and O. When amorphous carbon, therefore, is caused to assume the gaseous condition and unite with a molecule of oxygen, there is liberated 29,000 calories, but after assuming this condition in which the molecule is no longer composed of the inert carbon molecule, a second grm. molecule of oxygen unites with the CO and liberates 67,000 calories additional. The second molecule of oxygen therefore liberates 38,000 calories more than the first molecule, and as the oxygen molecules were alike this energy represents the bond uniting the carbon atoms and the energy necessary to break down the bond between these atoms and produce a gaseous condition from the amorphous condition.

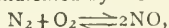
Returning to the nitrogen molecule, it is apparent that the formation of the grm. molecule of NO requires 21,500 calories in comparison to carbon liberating 29,000 calories to form CO; that is, the nitric oxide reaction is endo-

thermic while the carbon monoxide reaction is exothermic. Upon adding a second molecule of oxygen to the nitric oxide to form the peroxide we find—



or 13,500 calories per gram. molecule are liberated after previously expending 21,500 calories to form NO. Since there is liberated only 13,500 calories, upon adding a second molecule of oxygen the net energy required to form NO₂ would be 8000 calories. The first molecule of oxygen required 21,500 calories, whereas the second required only 8000 calories, so that 13,500 calories were required by the nitrogen molecule to prepare it for combination with the oxygen.

Dynamic Equilibrium.—These heats of combination developed by the atoms combining upon themselves indicate a very stable or inert molecule, and in liberating this energy to assume this more stable form the forces exerted are of large magnitude. It is readily apparent from this, for instance, how carbonaceous gases can readily form soot and cinders and other amorphous forms when the union with oxygen is disturbed, as the tendency of the atoms to unite with oxygen or to form carbon molecules will depend upon an adjustment of the surrounding conditions. This ever-changing condition of equilibrium constitutes the dynamic conception of equilibrium displacing the static equilibrium of the older theories of chemistry. In order to more carefully consider some of the theories that have been advanced it may be of interest to follow further some of the concepts of physical chemistry. The fact that the nitrogen atom has this strong tendency to combine upon itself with a liberation of energy greater than the combination with the oxygen atom indicates that in any reaction, when the combination with oxygen has made possible a changing of the atoms, there will be continuously in progress an action and a reaction, and the equilibrium will be indicated by the expression—



the sign of equality being displaced by the two arrows indicating that the action proceeds in each direction; that is, it is a reversible reaction, and the equilibrium will be dependent upon conditions, the two most important conditions being temperature and the active masses of the substances present. Considering, first, the effect of the active masses present, if it be assumed that the collision of molecules causes the rearrangement of the atoms comprising the molecule, and that of these collisions only a certain number will cause the rearrangement to proceed in one direction, the rearrangement will be greater the more frequently the collisions take place, there being some ratio for each individual case, and the collisions possible will obviously be proportional to the concentration present—that is, the collisions will be proportional to the number of molecules present. With two substances present, the collisions will be proportional to the molecules of each present and hence to their product.

(To be continued).

Attempts to Prepare Closed-Chain Compounds Analogous to Indazoles by means of Nitrated and Bromonitrated *o*-Anisidines.—E. Noelting and F. Steimle.—By the elimination of acid or water the diazoic salts and the free diazo-compounds of substituted orthotoluidines give closed-chain compounds, the indazols. It seemed not improbable that by using the diazoic derivatives of substituted orthoanisidines analogous compounds containing an extra oxygen atom would be obtained. The authors found, however, that this is not the case. When the diazoic compounds of the nitrated or bromo-nitrated anisidines are decomposed normally into phenols the quantity of nitrogen liberated corresponds to two atoms, while if derivatives with closed chains were formed it would be less, or even none at all, according to the proportion of cyclic derivative obtained.—*Bull. Soc. Chim. de France*, xvii.-xviii., No. 19—20.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY (LONDON SECTION).

Ordinary Meeting, January 3, 1916.

Mr. ARTHUR R. LING in the Chair.

Of the following papers those marked * were read:—

* "*Action of Boiling Acetic, Propionic, and Butyric Acids on Aluminium. with a Note on the Action of Formic and Some Higher Acids.*" By RICHARD SELIGMAN and PERCY WILLIAMS.

The experiments described in the paper were carried out to clear up certain anomalies in the literature on the action of acids on aluminium. Prominence is given to the action of boiling concentrated acetic acid on aluminium on account of the fact that whilst aluminium stills used for a number of years for distilling acetic acid have in general given satisfaction, certain parts are liable to corrosion. With the development of the colour industry in Great Britain this question became important.

The authors were at first inclined to attribute the phenomena to the presence or absence of air, but their investigation has shown, that, whilst ordinary concentrated acetic acid is almost without action on the metal, the acid if perfectly anhydrous attacks aluminium with great violence. As little as 0.05 per cent of water is sufficient to stop this reaction. The same applies to propionic and butyric acids.

The authors conclude from these facts that where aluminium plant is used in connection with the lower fatty acids, precautions must be taken to prevent these from becoming absolutely anhydrous, either by avoiding undue dephlegmation, or by introducing a trace of water vapour at the threatened points.

In the course of their work the authors obtained new aluminium salts of the acids examined.

* "*Action of Certain Chlorinated Hydrocarbons on Some Metals.*" By SOSALE GARALAPURY SASTRY.

Certain chlorinated hydrocarbons in the presence of moisture and under the influence of heat are liable to hydrolysis, especially if they are impure.

Carbon tetrachloride, dichloroethylene, trichloroethylene, tetrachloroethane, and pentachloroethane were examined. Many such compounds are used to extract oils and fats from vegetable seeds, and experiments were conducted in which the solvents, with and without seeds, were heated under a reflux condenser, in presence of strips of metals ($1\frac{1}{2}$ inches by $\frac{1}{2}$ inch), the heating being continued for ten hours. The metals were weighed before and after the experiment. Wrought iron, mild steel, nickel, copper, aluminium, and lead were examined, and tables are given in the paper showing the effect of the chlorinated hydrocarbons on them.

Tetrachloroethane and pentachloroethane hydrolysed most readily, and aluminium was the most easily attacked of all the metals. The author comes to the conclusion that dichloroethylene and trichloroethylene are the safest of these solvents now on the market.

* "*Viscosity of Oils in the Redwood and Ostwald Viscometers.*" By CHARLES A. SAVILL and ARTHUR W. COX.

This work was undertaken with a view to proving the connection existing between viscosities given by the Redwood viscometer (the one used in commerce) and the "absolute" type, and also of suggesting a simple method of conversion the one to the other.

The viscosities of a series of oils have been ascertained in the Redwood and Ostwald viscometers and it is found that the two sets of results of any oil when plotted on a graph give parallel curves. It is, therefore, evident that

Redwood and Ostwald viscosities are easily interconvertible, and, incidentally, that Redwood viscosity depends directly on the lubricating value of the oil. The results of the series of oils in both instruments are then taken and those obtained in one instrument plotted along one axis of a graph, and those in the other along the other axis. By reference to this graph it is then a simple matter to convert viscosities determined in one instrument into the corresponding figures in the other.

* "Estimation of Carbon Dioxide in Air by Haldane's Apparatus." By ROBERT C. FREDERICK.

For the estimation of small quantities of carbon dioxide in air this is the most convenient apparatus to use, and in skilled hands it is a quick and sufficiently accurate method. The principle is that the CO_2 is absorbed by caustic potash and the consequent diminution in volume, being measured on the graduated scale, gives a direct reading of the quantity present per 10,000 parts of air. If the potash solution is coloured with methyl orange movements of the liquid are made more apparent. Stress is laid on the importance of agitating the water in the water jacket, and considerable effort is avoided if a blowing bulb is used to provide the air current instead of blowing by mouth. A full and detailed account of the manipulation of the apparatus is given both when employed direct in the space to be tested and when used for the testing of air samples; in the latter case, a mercury bath is required. The sample bottles are two ounce, narrow-mouth stoppered, and the sample is collected by placing a rubber tube in the bottle and drawing a deep breath through the tube. A simple device is described for making the ordinary Haldane apparatus record up to 500 parts per 10,000 instead of 100, and also a labour-saving apparatus for propelling the mercury reservoir which prevents the mercury and potash being brought together accidentally and has other advantages.

"Method for the Determination of Free Alkali in Soap."

By F. H. NEWINGTON.

The method is based upon the principle of salting out the soap from its aqueous solution by means of sodium sulphate. Any free caustic alkali is thus obtained in aqueous solution together with the sodium sulphate after the soap has been removed.

The caustic alkali in this solution is titrated with $\text{N}/10 \text{ H}_2\text{SO}_4$ using a 5 per cent solution of silver nitrate as a spot indicator. With care the method will detect with accuracy 0.1 per cent of free sodium or potassium hydrate in either toilet, household, or soft soap. Silicates and borates do not interfere.

Exhibits.

Mr. C. A. HILL exhibited some preparations of analytical reagents, and in the course of a description of them explained the methods he had adopted in purifying them to meet the requirement of the specification laid down by the Joint Committee Institute of Chemistry and the Society of Public Analysts.

Mr. SHERARD COWPER-COLES sent an exhibit of lead-lined vessels.

Dr. E. C. B. WILBRAHAM exhibited and described natural and synthetic succinates.

Mr. T. D. MORSON (Hon. Sec.) exhibited and described glass filter cloths suitable for filtering corrosive liquids.

Exhibits of British glass chemical apparatus were made by Messrs. J. MONCRIEFF, Ltd., of Perth, and by Messrs. BAIRD & TATLOCK, Ltd., of London. Dr. Travers gave a brief description of Messrs. Baird & Tatlock's manufacture, which has been put on the market under the name of "Duro" glass. Both these makes of British glass are said to be equal in their resistance towards chemicals to Jena glass.

Messrs. DOULTON & Co. sent an interesting exhibit of porcelain ware for chemical purposes.

NOTICES OF BOOKS.

Relativity and the Electron Theory. By E. CUNNINGHAM, M.A. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1915.

IN this monograph the relation of the principle of relativity to the electron theory is explained with as little mathematical analysis as possible. The modifications which the principle has forced upon our notions of space, time, and motion are first discussed at some length, and modern ideas concerning momentum and energy are explained. The general conclusions to be based upon the principle of relativity are summarised, and the question of the existence of an objective ether is discussed. The author has condensed his material and provided a comparatively complete survey of his subject, but in so doing he has, no doubt unavoidably, made the book rather difficult to read and follow, and it seems doubtful whether the general reader, spoken of in the preface, will be able to make much use of it, though physicists and those who know something of the work of Lorentz and Einstein will find it a useful summary.

Historical Introduction to Chemistry. By T. M. LOWRY, D.Sc., F.R.S. London: Macmillan and Co., Ltd. 1915.

It may well be believed that the course of work given in this book has been proved by experience to be both interesting and instructive to all classes of students, as stated in the preface. The author has in his mind particularly the mixed classes in training colleges and medical schools, some of the students being beginners, while others have a considerable knowledge of elementary chemistry. For such classes the historical method is undoubtedly the best, and this book provides just what they need, and will moreover be found very valuable by teachers. It gives an account of classical experiments and theories often in the actual words of the original descriptions, and contains many illustrations of the apparatus used by early workers in the science. It is divided into two parts, the first dealing with the discovery of the facts of chemistry, while Part II. discusses chemical theories, beginning with a full treatment of the atomic theory. In both parts recent work is included; thus some account is given of Moseley's investigation of the high frequency spectra of the elements. Short summaries of each chapter are provided, and a bibliographical index is included, which gives in tabular form, with dates, lists of the works of the most prominent investigators.

Cuadro Sinoptico de la Doctrina Biocosmica de la Gravitacion Universal y de la Generacion de los Mundos. ("Synoptic Table of the Biocosmic Doctrine of Universal Gravitation and of the Generation of Worlds"). By Dr. ARISTIDES FIALLO CABRAL. Santo Domingo: La Cuna de America, Vuida de Roques and Cia. 1915.

IN this thesis a series of cosmic problems is stated, such as, "What is contained in interplanetary space?" "What are the comets?" "What is the origin of life upon our planet?" and the answers and explanations given by the classical theories are briefly stated as well as those provided by the biocosmic theory. These latter, which usually take the form of dogmatic assertions, are given at some length, but no attempt is made to state what the author's premises are, nor how much is to be regarded as deduction from untested hypotheses. The author possibly wishes the table to be regarded as providing a statement of debatable questions for further argument, and thus deliberately refrains from enlarging upon reasons and proofs.

CORRESPONDENCE.

GROWING MEDICINAL HERBS.

To the Editor of the Chemical News.

SIR,—It has been decided to start an organisation for growing medicinal herbs in this country, to be called the Herb-growing Association, affiliated to the Women's Farm and Garden Union.

Members may join on payment of 2s. 6d. per annum. Those who already belong to the Women's Farm and Garden Union may join on payment of 1s. per annum. These terms are for original members, and may be altered later.

Members will be entitled to advice on herb-growing and the preparation and disposal of herbs. By co-operation the growing of different herbs will be regulated so that the market may not be overstocked with some and be short of others.

Anyone wishing to help in the development of this industry and to hear details of the proposed working of the scheme is requested to communicate as soon as possible, as it is now that the supply from Central Europe is stopped that it is possible to keep the industry in this country.

Communications should be addressed to the Secretary of the Herb-growing Association, 45 (6), Queen Anne's Chambers, Westminster, S.W.

Hoping you will kindly give publicity to this organisation, we are, &c.,

EDITH L. CHAMBERLAIN, F.R.H.S.,
ALICE SANDFORD,

Members of the Herbal Sub-Committee.

LIQUID SMOKE.

To the Editor of the Chemical News.

SIR,—Would you kindly assist me through the medium of your journal to get in touch with manufacturers of "liquid smoke," a liquid which I have been given to understand is used in the process of curing bacon and hams by persons interested in this business in New South Wales. —I am, &c.,

KENNETH WATSON.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

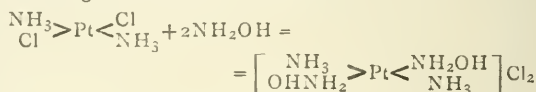
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 21, November 22, 1915.

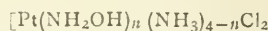
Action of Saccharose on Cupropotassic Liquid.—L. Maquenne.—The action of cupropotassic liquid upon saccharose at the temperature of boiling water is quite different from its action on invert sugar. The latter is attacked chiefly by the caustic alkali which the reagent contains, and the action is slightly dependent only upon its richness in copper, whereas saccharose is greatly affected by the latter, its reducing power increasing very rapidly with the quantity of dissolved metal. The duration of boiling also has an influence, and in order to investigate the reaction thoroughly the author used the same reagents always and kept the volume of liquid as low as possible, in order that the heating could be better regulated. He constructed a curve, taking the weights of sugar as the abscissæ and the corresponding reductions as ordinates, and observed that at first it rose very rapidly, then had a point of inflection, became horizontal, and finally fell. Thus, after a certain

concentration has been reached, the sugar exercises a protective action upon itself and accumulates. With glucose or invert sugar the curve is very nearly a straight line, and the precipitation of the copper soon becomes total for a given quantity of reducing sugar.

Hydroxylamine Complexes of Divalent Platinum.—L. Tschugaëff and J. Tschernjaëff.—When Peyrone's chloride is digested with hydroxylamine in aqueous solution the compound $[(\text{NH}_3)_2\text{Pt}(\text{NH}_2\text{OH})_2]\text{Cl}_2$ is readily obtained. It yields the complex $\text{NH}_3 > \text{Pt} < \text{NH}_2\text{OH}$ by the action of hydrochloric acid at the temperature of the water bath. This readily fixes two molecules of hydroxylamine to give $[\text{Pt}(\text{NH}_2\text{OH})_3\text{NH}_3]\text{X}_2$ and two molecules of ammonia to give $[\text{Pt}(\text{NH}_2\text{OH}(\text{NH}_3))\text{X}_2]$. By the action of hydroxylamine in aqueous solution on Reiset's base the following transformation is effected:—



All the representatives of the series—



are colourless substances more or less soluble in water. Measurements of the molecular conductivity give values which correspond exactly with those of electrolytes of the type $[\text{Pt}_4\text{A}]\text{X}_2$.

Bulletin de la Société Chimique de France.

Vol. xvii.-xviii., No. 19-20, 1915.

Some Colour Reactions of Triphenylmethane Derivatives.—E. Noelting and A. Kempf.—Bayer and Villiger have shown that triphenyl carbinol dissolves in concentrated sulphuric acid, giving an intense orange coloration. This is due to the formation of a salt, the triphenyl carbinol group possessing feeble basic properties. If the hydroxyl or methoxyl groups are introduced into the triphenylcarbinol the coloration is increased in intensity and the basic properties of the complex are accentuated, the OH group having the stronger influence. Rosolic acid and its hexamethoxy derivative both behave like basic dyes, and trianisylcarbinol has the same action. The authors have prepared the carbinol corresponding to phenyl-deorthomethoxyl-cresylmethane by oxidising the leucoderivative with lead dioxide in acetic solution, and the paracresol derivative similarly. The former gives a red coloration with sulphuric and the latter a Bordeaux red colour. If amino groups are introduced into triphenylcarbinol in the para position with reference to the original carbon basic carbinols are obtained which give strongly coloured salts, dyeing silk, &c., with a molecule of acid.

MEETINGS FOR THE WEEK.

TUESDAY, 18th.—Institution of Petroleum Technologists, 8. "Oil Storage," by H. Barringer.

— "Royal Institution, 3. "The Physiology of Anger and Fear," by Prof. C. S. Sherrington.

WEDNESDAY, 19th.—Royal Society of Arts, 4.30. "The Common Lands of London—the Story of their Preservation," by Lawrence W. Chubb.

THURSDAY, 20th.—Royal Institution, 3. "The Utilisation of Energy from Coal—The Chemistry and Economics of Coal and its By-products," by Prof. W. A. Bone.

— "Chemical, 8. "The Colouring Matter of Cotton Flowers," by A. G. Perkin. "Studies on the Oxidation of Unsaturated Fatty Oils and Unsaturated Fatty Acids—Part I. Formation of Acrolein by the Oxidation of Linseed Oil and Linolenic Acid," by A. H. Salway. "Synthesis of Keto-indo-pyrans," by S. G. Sastry and B. Ghosh. "Vapour Pressure of Glycerol Trinitrate (Nitroglycerin)," by A. Marshall and G. Peace.

FRIDAY, 21st.—Royal Institution, 4.30. "Problems in Capillarity," by Prof. Sir James Dewar.

SATURDAY, 22nd.—Royal Institution, 5. "Raphael and Michael Angelo," by C. J. Holmes.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2930.

FIXATION OF ATMOSPHERIC NITROGEN.*

By LELAND L. SUMMERS.

(Continued from p. 22).

The Velocity Coefficient.—If C_1 and C_2 represent the special concentration of gm.-molecules present, the velocity of the reaction will be proportional to $C_1 C_2$, or the velocity V of the reaction will be—

$$V = C_1 C_2 k;$$

where k is a constant or coefficient to be determined for the given temperature. This velocity of reaction will proceed each way in reversible reactions, the concentrations of the molecules in the reverse action being represented by C_1' and C_2' and the velocity of reaction by V' , the velocity of the reaction in the reverse direction will be—

$$V' = C_1' C_2' k';$$

where k' is the velocity constant to be determined for the reverse reaction.

The Equilibrium Constant.—The chemical driving force for any reaction will continually diminish as the reaction approaches equilibrium, or the velocity of the reaction will diminish as equilibrium is approached, and when equilibrium is reached V will equal V' and—

$$k C_1 C_2 = k' C_1' C_2'.$$

This dynamic equilibrium indicates that as much reactive substance is being formed in a given time as is being decomposed, and a fixed relation therefore results, but the reactions have not ceased, only the velocities have equalised, and the driving chemical forces are incapable of making any further change in the reacting substances unless the velocity in one direction or the other is changed. In this state of equilibrium the ratio between the velocity coefficients or constants is—

$$\frac{k_1}{k} = \frac{C_1' C_2'}{C_1 C_2} = K \text{ equilibrium constant.}$$

Or, as the concentration or active mass in any reaction increases, the velocity coefficient increases, and for each change in equilibrium due to temperature change there is a definite concentration ratio represented by this equilibrium constant K .

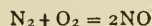
Partial Pressures.—If the concentration of a given molecule is C and the collisions of the molecule are proportional to this concentration, if there are two molecules the collisions between the two similar molecules will be C times as great as one molecule, or C^2 . As the total pressure of a mixture of gases is the sum of the pressure of each gas, and by Avogadro's hypothesis the pressure is proportional to the number of molecules in the given space, the concentrations, instead of being represented by gm.-molecules C , may be expressed as partial pressure p , and equilibrium will be represented by the ratio of the partial pressures of the gases. Thus two molecules of NO will have the pressure p_{no}^2 , while p_n and p_o may represent the pressure of the N and O. At equilibrium the constant K will then become—

$$K = \frac{p_{no}^2}{p_n p_o}$$

and for any pressure and volume the familiar equation—

$$PV = RT$$

will represent the work done. Where P is the pressure, V the volume, R the gas constant, and T the absolute temperature. The work done in the reaction—



will consist in taking one molecule of N from the pressure p and transferring to the pressure P also one molecule of O from the pressure p , to pressure P , and offsetting this work will be the transferring of two molecules of NO from pressure P_{no} to p_{no} , when the pressure of a gas at constant volume is increased by the infinitely small amount dp , the corresponding work done dA will be—

$$dA = dpV.$$

The Maximum Work.—If we substitute for V its value from the equation—

$$pV = RT$$

we have—

$$V = \frac{RT}{p}$$

and—

$$dA = \frac{RT dp}{p}$$

and for the work done between the limits of pressure p and P we have—

$$A = RT \int_p^P \frac{dp}{p} = RT \ln \frac{P}{p};$$

where $\ln$ is the natural logarithm. For the work done in forming the NO at a temperature T , we will have—

$$A = RT \ln \frac{p_n}{P_n} + RT \ln \frac{p_o}{P_o} - 2RT \ln \frac{p_{no}}{P_{no}};$$

or, simplifying and assembling the initial pressures and the final pressures in separate terms, we have for constant temperature—

$$A = RT \ln \frac{p_n p_o}{p_{no}^2} + RT \ln \frac{P_{no}^2}{P_n P_o}.$$

But the first term represents the initial pressures or the work done on the initial condition of the materials, and we are not called upon to furnish this energy, the change of energy being represented only by the second term—

$$RT \ln \frac{P_{no}^2}{P_n P_o}.$$

This quantity $\frac{P_{no}^2}{P_n P_o}$ is, however, the ratio of pressures

or concentrations represented by the equilibrium constant K , and hence the work done at any given temperature may be represented by the equation—

$$A = RT \ln K.$$

van't Hoff has applied this type of fundamental equation to a wide range of reactions, and by means of the second law of thermodynamics has made it applicable to temperature and concentration changes in which the latent energy plays an important part, for in these reactions the product of the specific heat by the temperature no longer represents the heat transfer.

van't Hoff's Fundamental Equation.—The second law of thermodynamics expresses the relation of A , the maximum work possible at a temperature T , and U , the decrease in energy of the system in relation to the ratio of change of A with the temperature T , the equation being—

$$A - U = T \frac{dA}{dT}.$$

Substituting in this the value of A and $\frac{dA}{dT}$ obtained from the equation—

$$A = RT \ln K,$$

we have when both A and $\ln K$ change with the temperature T —

* Paper presented at a joint meeting of the American Institute of Electrical Engineers and the New York Section of the American Electrochemical Society.—From the *Chemical Engineer*, xxi., No. 6.

$$\frac{dA}{dT} = R \ln K + RT \frac{d \ln K}{dT},$$

and hence—

$$U = -RT^2 \frac{d \ln K}{dT},$$

which is van't Hoff's fundamental equation for chemical reactions in which the heats of reaction U are important factors, and both the temperature and concentrations may be variable. The quantity U , which in thermodynamics represents the decrease in energy of the system, may here represent the energy of chemical combination, which changes very little with changes of temperature and is generally designated Q , and in the case of nitric oxide it has the value 21,500 calories per gram-molecule; so the equation becomes—

$$43,000 = -RT^2 \frac{d \ln K}{dT},$$

and when using the air as a source of nitrogen in which the nitrogen content is 79.2 per cent and the oxygen 21.8 per cent, and letting x represent the percentage of NO formed, as one-half x will be from the nitrogen and one-half x from the oxygen, the equilibrium constant K will be—

$$K = \frac{x^2}{\left(79.2 - \frac{x}{2}\right)\left(20.8 - \frac{x}{2}\right)}.$$

Nernst's Determinations of Equilibrium.—Nernst and his assistants determined x for a number of temperatures, the calculated and observed values being as follows:—

T.	x (obs.)	x (calc.)	Observer.
1811	0.37	0.35	Nernst.
1877	0.42	0.43	Jellinek.
2023	Between 0.52 and 0.80	0.64	Jellinek.
2033	0.64	0.67	Nernst.
2195	0.97	0.98	Nernst.
2580	2.05	2.02	Nernst-Finckh.
2675	2.23	2.35	Nernst-Finckh.

Nernst's calculations of x or equilibrium volumes in per cent of NO, using air at temperature of 1500° T to 3200° T, are plotted in Fig. 1.

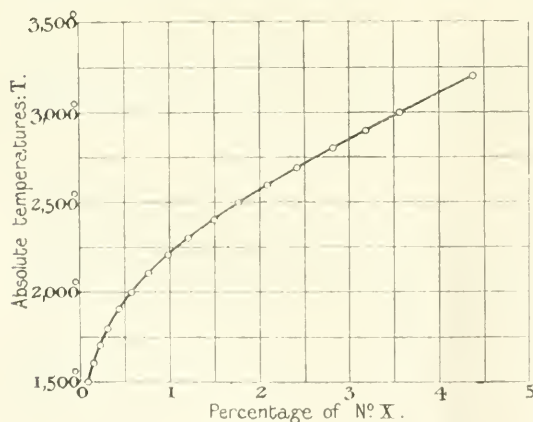


FIG. 1.

Rapidity of Dissociation.—Nernst and Jellinek also determined the rapidity with which the NO is decomposed or dissociated at the various temperatures, and these experiments showed that the tendency of NO to revert to molecular N and O is very slight below a temperature of 1500° C., but increases very rapidly with the temperature, so that the time of withdrawing the products through the varying zones of heat in the electric arc is sufficient to

effect a large amount of dissociation. In order to avoid this dissociation a rapid movement of the air through the arc or the arc through the air is desirable, and this in turn causes increased radiation and convection losses, so the maximum possible temperature of the arc is not obtained, and hence there are imposed very distinct limitations to the yield of NO.

Haber's Theory of Ionic and Electronic Collisions.—Haber and Koenig investigated the possibility of utilising lower temperatures in the arc to avoid dissociation by enclosing the arc in a water-cooled quartz tube, whereby moderate temperatures were preserved. In place of the molecular collisions we have assumed above as due to the thermodynamic condition of the gas, they used a vacuum and endeavoured to utilise the kinetic energy from the rapid motion of the ions and electrons liberated by the arc stream under these conditions. Haber considered it possible to increase the thermodynamic concentrations about 50 per cent. His tests indicated that using a temperature of 3000° C. it was possible to show 10 per cent concentrations of NO, which would correspond to a temperature under the thermodynamic equilibrium of 4300° C. Haber gives a table showing the effect of various mixtures of N and O when working with the increased mean free path of the molecules due to a vacuum of 100 mm. of mercury. In his work Haber prefers to use the square root of the equilibrium constant K we have used above, thus enabling the partial pressures of the resulting substances to be read direct, while the partial pressures of the ingredients are expressed as square roots of the pressures.

Haber's table for a pressure of 100 mm. is as follows:—

	Gas mixture.			$K = (NO) \cdot (N_2 \frac{1}{2} (O_2) \frac{1}{2})$	Thermodynamically calculated absolute temperature by	
	O ₂ , per cent.	N ₂ , per cent.	NO, per cent.		Haber.	Nernst
Air	20.9	79.1	9.8	0.284	4365	4334
Half-half mixture ..	48.9	51.1	14.4	0.337	4686	4650
Reversed air mixture ..	44.4	55.6	14.3	0.337	4686	4650
.. ..	75.0	25.0	12.8	0.357	4805	4767
.. ..	81.7	18.3	12.1	0.397	5042	5000

The yields of NO per kilowatt hour obtained by Haber were unsatisfactory, and the complications of small water-cooled tubes and working under a vacuum of 100 mm. have not justified commercially the higher concentrations of NO he obtained.

Commercial Processes now in Use have Distinct Limitations.—We may assume that up to the present the processes in commercial use are limited strictly by the thermodynamic equilibrium of the van't Hoff equation. As the volume of gases when working with low concentrations of NO are considerable, the radiation and convection losses as well as the transfer of sensible and latent heat from the arc to the gases lower very materially the temperature of the arcs, and the yields therefore indicate an average working temperature of 2200° C. to 2500° C., or concentrations of 1.5 per cent to 2 per cent NO when working with air. These theoretical limitations of the direct processes of forming NO have therefore led to many efforts to dissociate the nitrogen molecule by other means.

Sources of Chemical Energy.—Naturally the sources of chemical energy have offered a most fruitful field, but, like the synthesis of carbon compounds, a considerable elevation of temperature is necessary before the chemical energy becomes effective enough to break the bond of the nitrogen molecule. At these elevated temperatures practically all elements or compounds which release sufficient energy to combine with nitrogen have a greater combining power for oxygen, so the processes cannot be conducted with air, but involve the separation of the nitrogen from the oxygen of the air as a preliminary step. The compounds of nitrogen thus formed do not therefore include

the oxides of nitrogen. The common elements exhibiting the most pronounced tendency to combine with nitrogen are calcium (Ca), magnesium (Mg), aluminium (Al), boron (B), &c. The carbides of a large number of metals also exhibit a pronounced tendency to combine with molecular nitrogen when heated.

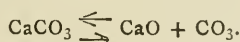
The great advantage from a theoretical standpoint in utilising these processes is that the reaction with nitrogen may be made more complete as equilibrium may be continually disturbed by withdrawing the compound of nitrogen formed or by presenting to the nitrogen to be combined fresh combining surfaces of the substance, and the action may be caused to proceed practically quantitatively, thus avoiding heating large quantities of materials which are inert to the reaction. A vast field of research is opened by these possibilities, as very few of the equilibrium figures have been determined, and it is almost certain that direct combustion methods may eventually be evolved along these lines.

The experimental data are so meagre that no theoretical limitations can be placed. The reactions assume unusual importance however on account of a wide application in the arts. This may be best illustrated by considering the formation of calcium carbide, CaC_2 , in relation to its three reversible reactions, namely,—

1. $\text{CaO} + 3\text{C} \rightleftharpoons \text{CaC}_2 + \text{CO}$
2. $\text{CaC} \rightleftharpoons \text{Ca} + \text{C}$
3. $\text{CaO} + \text{C} \rightleftharpoons \text{Ca} + \text{CO}$

There are here six substances, some in solid form, some in liquid, and some gaseous (molecular and atomic), and it is evident that the temperature will have a marked influence on the equilibrium which will exist, and the reaction will be greatly affected by very minute changes, for the partial pressure of the gases will be suddenly changed by such conditions as the carbon released in a gaseous state immediately combining to form amorphous carbon, or the metallic calcium vapour combining with the oxygen released by the CO to form calcium oxide, which immediately precipitates as a solid. The fact that calcium oxide, which is most refractory, can be vaporised at a temperature of 1600°C . to 1800°C . in the sense that the calcium is vaporised and decomposes CO to again precipitate CaO, is one of the actions similar to the fumes in smelting furnaces which accounts for a heavy loss of metal at temperatures not ordinarily capable of producing vapours. When nitrogen is inserted in a reaction of this kind, there are immediately formed complex carbon-nitrogen compounds, but the action of the oxygen present is to dissociate these, allowing the nitrogen to combine into the molecular form and the metal to precipitate from the fume as a minute particle of metallic oxide, the carbon precipitating as amorphous carbon in the form of soot, as all of these reactions liberate a large amount of energy. The temperature of these reactions is from 1500°C . to 2000°C ., and is therefore well within the range of combustion methods if the combustion could be in contact with the substances as in the blast furnace, but the presence of the oxygen necessary for combustion prevents the formation of nitrogen compounds.

The effect of partial pressures in these reactions is of fundamental importance. The active mass of a solid is constant, and hence at the boundary surface where the solid and gases meet there is a high velocity of reaction. Equilibrium will be produced either by the solid forming a coating of the compound which will place it in equilibrium or by the pressure of the gases generated from the reaction producing a condition of equilibrium. Taking the familiar calcium carbonate reaction as an illustration,—



There being two substances in the solid state and one in the gaseous, the equilibrium constant K will be—

$$K = \frac{\text{CaO} \times \text{CO}_2}{\text{CaCO}_3};$$

where CaO and CaCO_3 are the very slight vapour pressures of the solids; that is, the sublimation pressures, which in practice are too small to measure. The pressure of the CO_2 will be practically the total pressure, and as this varies, the velocity constant K will vary and hence for any temperature there is but one pressure for equilibrium. Le Chatelier measured the temperatures and pressures of the above reaction over a wide range and found a variation in the temperature necessary to produce the reaction of from 547°C . at 27 mm. pressure to 865°C . at 1333 mm.; or in other words, equilibrium could be produced through a range in temperature of 60 per cent, and at one point a change of two degrees necessitated a change in pressure of over 10 per cent in order to restore equilibrium. Rothmund found the equilibrium pressure of CO in the carbide of calcium reaction to be 250 mm. at 1620°C . If the CO pressure was raised above the equilibrium figure at this temperature, CO was absorbed and no carbide was formed. By inserting inert gases so the CO was diluted and its partial pressure reduced, the temperature of the formation of carbide was varied over 20 per cent. These results all indicate that for the nitrogen reactions must not only be subject to accurate temperature regulation, but the partial pressures must be controlled, and it is probable that definite zones of reaction must be maintained. The present commercial applications such as the Serpek and cyanamid processes prepare the compounds of nitrogen by causing the nitrogen to react largely with the solid masses, and thus avoid many of these complications due to the vapour processes, or variable minute pressures of sublimation.

By substituting the resistance furnace for the arc and reducing the metals in the presence of nitrogen, thus forming nitrides or forming carbides, and treating these in the presence of nitrogen, there have been developed a number of processes which have been commercially applied.

(To be continued).

PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF FLUORIDES. THE ANALYSIS OF SILICATES AND CARBONATES FOR THEIR FERROUS IRON CONTENT.*

By O. L. BARNEBEY.

(Concluded from p. 19).

Notes on the Method.

1. SCRUPULOUS care must be exercised to exclude the air when decomposing the silicate with hydrofluoric acid in order to prevent oxidation. However, after the addition of the boric acid the ferrous solution becomes quite stable.

2. A carbon dioxide generator, after filling with carbonate (marble) and acid, should be allowed to generate carbon dioxide for a considerable period of time to remove the air as completely as possible. (Heating magnesite would probably be a still better method for obtaining carbon dioxide). Only recently boiled water should be used in the water-bath and only recently boiled distilled water added to the sample.

3. Until accustomed to the method of analysis the analyst should always check his procedure by heating measured volumes of standard ferrous iron solution with hydrofluoric acid, and titrating with the same manipulation as in the analysis, in order to ascertain if the air is being excluded effectively.

4. Filtration is desirable when solid organic matter is

visible after the sample is thoroughly decomposed. Filtration may not remove all the influence of the organic matter, however. The soluble organic matter naturally still has opportunity to give a reducing effect. If the clear solution is slightly coloured by the presence of organic matter it should be largely diluted and titrated to the first distinct pink tinge of the solution. The presence of organic matter makes the end-point much less stable than in its absence. Another procedure can be substituted for filtration. The sample can be transferred to a volumetric flask, diluted to the mark and the residue allowed to settle, after which portions can be withdrawn with a pipette and titrated.

5. Instead of adding solid boric acid the fluoride solution can be poured directly into an excess of a saturated solution of boric acid.

6. A convenient strength of permanganate for titrating samples low in ferrous iron content is 1 cc. = 0.001 grm. FeO.

Samples 1—5 inclusive (Table XII.) contained no organic matter and were free from sulphides. The end-points were fleeting in analyses 2a, 3a, and 4a, especially the last two. Samples 6—8 inclusive contained considerable organic matter. In analysis 6a the result is only approximate, as the end-point was very fugitive because of the organic matter present. In 6b, 6c, 6d, 6e the solutions were filtered, as also were the samples 7b and 7c as well as 8b and 8c. Larger portions could have been used to advantage in Samples 5, 7, and 8. Samples were not analysed according to procedure "a" for 7 and 8 because of the presence of large amounts of organic matter. Naturally filtration of the hydrofluoric acid solution is not advisable on account of the rapidity of oxidation of ferrous iron in such a solution by the air and also because of the action of the solution on glass.

TABLE XII.—Analyses of Silicates for Ferrous Iron.
(1 cc. $\text{KMnO}_4 = 0.001$ grm. FeO).

No.	Sample. Grms.	Per cent FeO.				
		a.	b.	c.	d.	e.
1.	4.0	0.12	0.08	0.10	—	0.08
2.	2.0	3.74	3.54	3.48	3.56	3.45
3.	1.0	6.94	6.49	6.45	—	6.50
4.	0.4	14.70	14.36	14.36	—	14.42
				14.48		
5.	2.0	0.09	0.084	0.085	0.078	0.080
6.	1.0	6.20	5.47	5.26	5.46	5.48
				5.46		
7.	2.5	—	0.51	0.51	—	—
8.	1.0	—	0.43	0.45	—	—

(a) Sulphuric and hydrofluoric acids used for decomposition. No boric acid was added.

(b) Decomposed like a. Boric acid was added.

(c) Hydrofluoric acid used for decomposition. Boric acid was added.

(d) Decomposed with hydrochloric and hydrofluoric acids. Manganese sulphate (80 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ per litre) and boric acid were added.

(e) Decomposed like d. Manganese solution I and boric acid were added.

The results obtained by decomposition methods b, c, d, and e are somewhat lower than those obtained by a, but they are believed to be more accurate. The author prefers the use of sulphuric acid with hydrofluoric acid for decomposition of a silicate whenever this method of attack is applicable, although hydrochloric acid with hydrofluoric acid or hydrofluoric acid alone can be used satisfactorily. The chlorine influence on the titration must always be removed when hydrochloric acid is utilised.

Naturally, when the above method is applied to the analysis of carbonate rocks the addition of hydrofluoric acid may be omitted if the sample is thoroughly decomposed by the other acids, or if only the iron existing as carbonate is desired. However, the hydrofluoric acid finds

application if considerable siliceous matter is present and the total ferrous iron content of the sample is wanted.

The action of these preventives may be classified as follows:—Class (a) removes most if not all of the active hydrofluoric acid by the presence of another acid through the medium of which the oxidation proceeds by virtue of its greater strength as an acid or by mass action. Sulphuric acid by conductivity measurements is stronger than hydrofluoric acid; phosphoric acid is much weaker. Hence sulphuric acid gives fairly good and phosphoric acid poor prevention. The acid salts found to be of worth are valuable mostly for their acidity, *i.e.*, NaHSO_4 , KHSO_4 . (b) Certain salts react with the fluorides present, forming undissociated fluorides and salts of other acids than hydrofluoric, through the medium of which the reaction proceeds. Examples of this class of preventives are ferric and magnesium sulphates. Phosphates are not desirable, inasmuch as they yield phosphoric acid by interaction with hydrofluoric acid, and phosphoric acid is to be avoided in the titration unless all the hydrofluoric acid is removed. Of the neutral phosphates only those of the alkalis are soluble in water; hence to add metal phosphates, either the solids or the phosphate dissolved in phosphoric acid must be added, thus forming acid phosphates in most instances and again bringing the phosphoric acid into predominance. Still another difficulty arises from the use of phosphates; sufficient acidity must be present to prevent ferrous phosphate from precipitating. If the ratio of phosphate to acid does not give sufficient acidity the titration is worthless, being low. Classes (a) and (b) are so closely related that they could properly be included in one class, but in (a) hydrofluoric acid is present and in (b) a fluoride. (c) Other reagents react with hydrofluoric acid in such a manner as to combine the fluorine in the anion which does not dissociate to yield hydrofluoric acid. Boric and silicic acids are such preventives, forming fluoboric and fluosilicic acids by interaction with hydrofluoric acid.

Of the preventives tried the author prefers boric acid. This acid can be obtained on the market in a high degree of purity and is a cheap commodity. It gives a solution which is clear. The solubility of boric acid in water peculiarly fits it for this purpose, being sufficiently high to allow a rapid reaction with hydrofluoric acid and yet not so high as to cause waste of the chemical when adding the solid in slight excess. The appearance of solid boric acid in excess likewise indicates that sufficient reagent has been added to react with the hydrofluoric acid present. This is a distinct advantage when titrating solutions containing unknown or variable quantities of hydrofluoric acid. Solid boric acid in excess is advantageous rather than detrimental in obtaining the end-point. The fluoboric acid solution of ferrous iron oxidises very slowly in the air, thus removing an undesirable feature of the titration accompanying the usual methods for determining ferrous iron. It gives the best prevention of the hydrofluoric influence during titration.

Summary.

1. This study confirms earlier work which has shown that the permanganate titration of ferrous iron in the presence of fluorides gives an unstable end-point, the instability increasing with increased concentrations of iron and hydrofluoric acid.

2. The use of sulphuric acid of normal to 5 N concentrations permits a good titration to be made in the presence of normal hydrofluoric acid. Phosphoric acid cannot be substituted for sulphuric acid, since the former yields a fugitive end-point. Certain acid sulphates accomplish the same result as the free acid.

3. Certain sulphates—*i.e.*, ferric and magnesium sulphates—react with the hydrofluoric acid and check its influence in the titration. Phosphates and acid phosphates are undesirable for prevention of the fluoride influence.

4. Certain oxides also have prevention tendencies—*i.e.*,

molybdenum trioxide and titanium dioxide, the titanium dioxide being the better. The hydrofluoric acid may combine with the titanium and molybdenum, forming simple fluorides or fluotitanic and fluomolybdic acids. Boric acid and silicic acid remove the hydrofluoric acid, forming fluoboric and fluosilicic acids. Boric acid is the most effective of all reagents studied.

5. Ferrous iron solutions containing fluoboric acid are quite stable in the presence of air.

6. The prevention of the reagents studied may be classified in three divisions: (1) addition of a stronger acid than hydrofluoric acid for the solution medium, (2) conversion to salts of other acids forming also undissociated or sparingly dissociated fluorides by mass action of the preventer, and (3) conversion of the hydrofluoric acid to a complex acid, which when dissociated gives a complex anion rather than the simple fluorine ion.

7. A modified procedure is given for the analysis of silicate or carbonate rocks for their ferrous iron content, using boric acid to remove the detrimental influence of the hydrofluoric acid.

ON THE COMBINATION OF PROTEIN WITH HALOGEN ACIDS.*

y J. H. LONG and MARY HULL.

(Concluded from p. 17).

THESE results are extremely interesting, as they show the extent of combination without the aid of heat. The final temperature of drying to constant weight in the electric oven was not over 75°, and this heat was not applied until all acid vapours had been absorbed in the desiccators. It will be seen that the results are very close to those secured by evaporating the acid and protein mixtures in the water-bath and drying at 105°.

It is evident, therefore, that the proteins and acids unite in this manner in proportions which are apparently definite, but not in proportion to the molecular weights of the acids. The power of combination is possibly connected with the volatility of the acid, since we find that HI unites with the proteins in proportion greater than does HBr, and this in turn greater than HCl. Nothing is shown in the HI column of Table XVIII. which would suggest that the halogen acid addition is accompanied by the loss of water; that is, no hydrolysis appears to have taken place, but the reaction follows, as would that between glutaminic acid and hydrochloric acid, for example. In the complex protein molecules there are many of these amino groups available, and the number of acid molecules which may be united to them apparently depends on the "strength" of the acid, as measured by its lower vitality.

Table XIV. discloses the important fact that we have a constant combination for the hydriodic acid when amounts above 15 cc. of the 0.2 N solution are used with 750 mgrms. of protein. For 1 grm. of each protein about 553 mgrms. of HI goes into combination, and this evidently represents a maximum under the conditions. When heat is applied much more may be held in some form.

These halogen acid combinations, whether made by simple action of the acid on the solid protein or by this treatment followed by evaporation, undergo a rather marked degree of dissociation by contact with water. The dry hydrochloride of egg albumin gives up its acid, and on this account the compound has been used to some extent as an aid to digestion. The rate of dissociation is, however, slow. Some information on this point is given in a recent publication from this laboratory in which the

hydrogen concentration of HCl separated from egg albumin was measured by the gas chain method (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1333). In the treatment of a given weight of a protein hydrochloride with successive equal volumes of water the acid strength of the dissociated portion gradually diminishes.

It has been shown above that the behaviour of hydriodic acid with protein when evaporated is different from the behaviour of the corresponding chlorine and bromine acids, but the combination as measured by indicator titration is of the same order, as shown by these results. Portions of the three substances corresponding to 750 mgrms. of dry protein were rubbed up in a mortar with 10 cc. of 0.2 N acid and washed into flasks with 10 cc. more. At the end of an hour the excess of "free" acid was found by 0.1 N alkali and methyl orange:—

TABLE XV.—Combination of HCl, HBr, and HI with 750 mgrms. of Proteins as described.

	Cc. 0.2 N HCl.	Cc. 0.2 N HBr.	Cc. 0.2 N HI.
Egg	3.4	3.0	3.8
Fibrin	3.5	3.7	4.5
Casein	2.2	2.1	1.5

In each case the fibrin seems to hold more acid and the casein less than the egg. We should expect the same volume of acid to be combined with the different proteins. The discrepancy is probably due to the lack in delicacy in the behaviour of this indicator in presence of undigested protein, but the results are close enough to show that the combinations are of the same type.

In place of titrating directly, similar mixtures were filtered and the residues on the filter washed with successive equal portions of water, 20 cc. in each case. These washings were titrated separately. It was found that the fibrin held the acids more tenaciously than the other proteins. In seven or eight washings about one-fifth of the hydrochloric acid could be removed from the egg, a tenth from the fibrin, and a fourth or less from the casein. The dissociation of the hydrobromic acid is of the same order.

The behaviour of hydriodic acid is most interesting here in view of the large weight held after evaporation experiments. The figures of Table XVI. show the amount of 0.2 N NaOH required to titrate the first filtrate and successive washings in experiments with egg and fibrin.

TABLE XVI.

Filtrate and washing.	Egg.		Fibrin.	
	a.	b.	a.	b.
	Cc.	Cc.	Cc.	Cc.
1st.	13.75	14.30	12.55	13.20
2nd.	1.90	2.25	1.55	1.90
3rd.	1.25	1.30	1.50	1.20
4th.	0.90	0.60	0.70	0.90
5th.	0.60	0.20	0.60	0.40
6th.	0.30	0.00	0.50	0.20
7th.	—	—	0.40	0.10
8th.	—	—	0.20	—
9th.	—	—	0.10	—
Total.. ..	18.70	18.65	18.10	17.90
Cc. 0.2 N HI held	1.30	1.35	1.90	2.10

It is seen that after the prolonged washings about two-thirds of the HI held by the egg is washed out and over half of that held by the fibrin, as measured by the direct titrations. While the procedure is lacking in quantitative accuracy it gives a good comparative result. It is evident that when heat is not applied the hydriodic acid is very loosely held. The type of salt produced in this way suffers extended dissociation by water.

* Presented at the New Orleans meeting of the American Chemical Society, April 2, 1915. From the *Journal of the American Chemical Society*, xxxvii., No. 6.

TABLE XIV.—Combination of Protein with HCl, HBr, and HI, and Evaporation at Low Temperature.

(The Equivalent of 750 mgrms. of Anhydrous Protein used in each case).

No.	Cc. 0.2 N HCl.	Mg. HCl.	Inc. in wt.	Mg. HCl held.	Cc. 0.2 N HBr.	Mg. HBr.	Inc. in wt.	Mg. HBr held.	Cc. 0.2 N HI.	Mg. HI.	Inc. in wt.	Mg. HI held.
1. Casein ..	30	219.0	73	71	30	485.7	265	270	30	768	429	426
2. Casein ..	25	182.5	81	72	25	404.8	274	268	25	640	400	415
3. Casein ..	20	146.0	74	70	20	323.8	294	271	20	512	468	420
4. Casein ..	15	109.5	73	73	—	—	—	—	15	384	382	371
Mean ..	..	..	..	71.5	Mean ..	..	..	269.6	Mean ..	..	..	420
5. Fibrin ..	25	182.5	71	63	25	404.8	289	280	30	768	450	430
6. Fibrin ..	20	146.0	65	62	20	323.8	272	280	25	640	402	311
7. Fibrin ..	15	109.5	69	63	15	242.8	272	274	20	512	405	404
Mean ..	..	..	..	62.6	Mean ..	..	..	278	Mean ..	..	..	415
8. Egg alb.	25	182.5	77	71	25	404.8	310	348	30	768	437	433
9. Egg alb.	20	146.0	77	73	20	323.8	292	310	25	640	487	416
10. Egg alb.	15	109.5	65	70	15	242.8	224	232	20	512	413	390
Mean ..	..	..	..	71.3	Mean ..	..	..	329	Mean ..	..	..	413

Resumé.

The experiments detailed above show that the amounts of the halogen acids which combine with casein, fibrin, and egg albumin, as measured by the usual indicator titration, are low and not accurately proportional to the molecular weights of the acids. The discrepancies are probably due to the lack of delicacy of the indicator in presence of unchanged protein, on the one hand, and to the more or less complete dissociation of the protein-acid compound on the other. The latter is doubtless the more important factor, since it has been shown that a large fraction of the acid may be washed away from the protein.

When the proteins named are treated with the halogen acids of 0.2 N concentration in excess, and the mixtures evaporated at a low temperature by standing over sulphuric acid some weeks, followed by similar treatment over solid alkali, and final drying to constant weight at 75°, very constant weights of acid are taken up and held by the protein. These weights of acid are not increased by the excess added, which points to the definite character of the reaction. The amounts are not proportional to the molecular weights of the acids, the combining proportion being relatively greater for HI than for HBr, and greater for the latter than for HCl. But the compounds all appear to be salts of the protein molecule, and contain many times as much acid as is suggested by the titration combinations. These dry salts undergo dissociation readily when mixed with water.

If the acid protein mixtures are evaporated on the water-bath in place of being dried at a low temperature the behaviour of HCl and HBr remains essentially the same. No greater amounts of the acid are taken up by a grm. of protein, and we doubtless reach here a maximum in the combining power of the acid and protein. A salt of a type different from that formed in solution at a low temperature is secured. In the case of the HI, however, there is no such limit to the iodine held, and it is probable that we have here a substitution of the element in the nucleus of the protein molecule as well as an addition of the acid. As much as 75 per cent of the weight of the original protein may be so held, and the combination has a brownish ochre colour, with loss of protein reactions.

PHYSICAL AND MECHANICAL FACTORS IN CORROSION.*

By CECIL H. DESCH, D.Sc., Ph.D.,
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It is generally recognised that the corrosion of a metal or alloy is intimately connected with the formation of local electrolytic couples at the surface in contact with the solution or atmosphere. The process of corrosion is always initially one of chemical solution, the dependence of which on electrolytic conditions is established. A highly purified specimen of zinc is almost inactive towards acids, whilst commercial zinc, containing lead, is rapidly attacked, the action of the acid beginning in the immediate neighbourhood of the lead particles. This is one of a large class of similar facts, the bearing of which on the question of corrosion is often overlooked. The object of the present paper is to show how the mechanical heterogeneity of metals and alloys affects the nature and velocity of the process of corrosion.

Laboratory tests of corrodibility are commonly made for the purpose of determining which of several materials will offer the greatest resistance to corrosion when exposed under certain specified conditions. As it is impracticable to reproduce these conditions exactly on account of the long duration of the tests, rapid tests, involving the use on the one hand of active chemical corroding agents, or on the other of an applied electromotive force, are commonly adopted. Such tests are usually of an unsatisfactory character. A number of metals or alloys, arranged in order of their resistance to acid solutions, will present a very different order when exposed to technical conditions, such as contact with town air or sea water.

Moreover, tests which involve the determination of the weight of material removed by the corroding agent, usually including that which is removed by brushing or scraping after corrosion, confound a number of successive changes in such a way that their separate influences cannot be disentangled. For example, experiments which determine

* A Contribution to a General Discussion on "The Corrosion of Metals," held before the Faraday Society, December 8, 1915.

the relative loss of weight of specimens immersed in an acid or salt solution for equal periods of time fail to distinguish between (a) the material actually dissolved and remaining in solution, (b) the loose, flocculent precipitate of basic salts which is produced in salt solutions, (c) the adherent film of basic salts which in some cases has the properties and effect of a tough, protective varnish, (d) the metallic layers, such as the spongy layer of copper formed in the "dezincification" of brass, and (e) crystals mechanically dislodged from the face of the specimen by



FIG. 1.—Corroded Surface of Rolled Duralumin (Multiplied 50 diam.).

solution of the material surrounding them. All these five products are removed when the specimen is brushed or scraped before re-weighing, but their relative quantity is not determined, although the power of a metal or alloy to resist corrosion depends in no small measure on the ratio between these quantities. From an examination of the surface after an experiment of this kind the corrosion is described as "general corrosion" or as "pitting," the

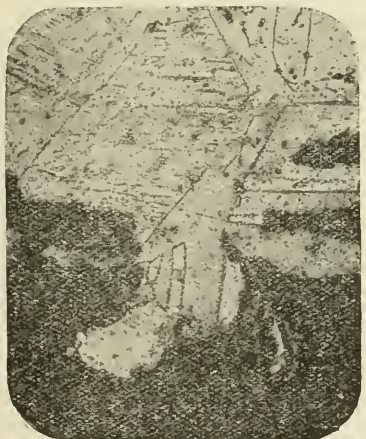


FIG. 2.—Transverse section of Dezincified Brass. (Multiplied 250 diam.).

latter referring to localised attack, the solution of the metal being either entirely limited to or greatly intensified in definite areas. Microscopical examination, however, often shows that what is apparently general corrosion is really pitting on a minute scale. An annealed brass exhibits true general corrosion, the surface being uniformly attacked, except that neighbouring crystal grains of different orientation may show slight differences of level. On the other hand a light aluminium alloy corrodes by

minute pitting, the pits bearing a definite relation to the arrangement of the micrographic constituents.

The heterogeneity which gives rise to the formation of local couples may be of two kinds, chemical or physical. A pure metal is of necessity chemically homogeneous in the sense that it is made up of only one kind of atoms, but it may be physically heterogeneous. A metal which has been "cold-worked," or deformed at a temperature below that at which complete recrystallisation takes place, con-

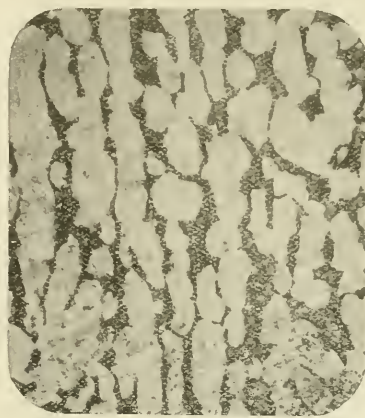


FIG. 3.—Muntz Metal in First Stage of Dezincification. (Multiplied 100 diam.).

tains, as shown by Dr. Beilby, films of amorphous material between the separate crystal grains. The amorphous metal is more electro-positive than the crystalline, as is shown by measuring the difference of potential between two specimens of the same metal in the cold-worked and annealed state respectively (W. Spring, *Bull. Acad. Roy. Belg.*, 1903, 1066), consequently cold-rolled metals almost always corrode in such a way that greater chemical action

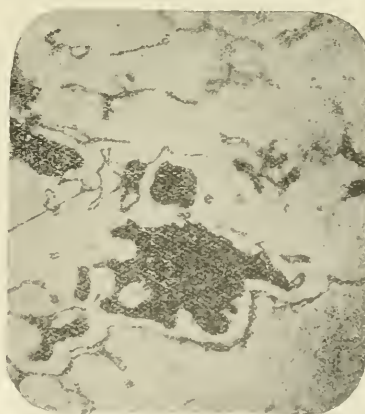


FIG. 4.—Pitting in Light Aluminium Alloy. (Multiplied 250 diam.).

takes place along certain lines than along others, such lines following the direction of the rolling. This effect is not to be confused with the striation observed on the surface of rolled plates due to the inclusion of impurities. Rolled sheet-iron will corrode in parallel lines even in the absence of cold-working, on account of the presence of particles of scale which are embedded in the surface during rolling and produce a heterogeneous structure. Cold-worked metals become striated during corrosion, however, even when the outer skin has been completely

removed before the test was made. Fig. 1 shows the corroded surface of a specimen of rolled duralumin, in which the lines of rolling are clearly indicated.

There are thus two reasons for the greater corrodibility of cold-worked than of annealed metals: the more electro-positive character of the former and their greater heterogeneity. Against this must be set the fact that some metals are commonly porous in the cast or annealed state, and that the closing of the surface pores by cold-rolling may increase the resistance to corrosion, in some cases more than compensating in this way for the electrochemical difference. This applies mainly to atmospheric corrosion; in contact with liquids the electrochemical differences assert themselves more strongly.

It is possible that even annealed metals of high purity may be minutely heterogeneous. Several observers (H. Heller, *Zeit. Phys. Chem.*, 1915, lxxxix., 761; E. Cohen and W. D. Heldermaun, *Ibid.*, 1915, lxxxix., 733; H. J. M. Creighton, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2064) have recently described the disintegration of lead in contact with an electrolyte. A specimen of sheet lead, immersed in a slightly acid solution of lead nitrate or acetate, gradually becomes loosened in texture, and is ultimately converted into a spongy mass of crystals, the metal being obviously dissolved and re-deposited. The writer has repeated this experiment several times, and finds that it is indifferent whether commercial sheet lead or the purest assay foil be taken. Cold-working is here excluded, as lead anneals itself spontaneously at the ordinary temperature. Whether lead be, as Cohen assumes, a mixture of stable and metastable allotropic modifications, of which the latter would tend to dissolve and recrystallise as the former, remains to be proved.

Local cold-working greatly accelerates corrosion. The severely cold-worked condition which prevails around a punched hole in a boiler-plate is always the spot at which corrosion first appears if opportunity offers. The contact of cold-worked and annealed metal in an engineering structure is for this reason undesirable.

Besides the physical condition of the metal, that of the product of corrosion has to be taken into account. When iron rusts the product is porous and bulky. It affords a ready passage to the corroding liquids or vapours, whilst at the same time, being strongly electro-negative to iron, the ferric oxide furnishes innumerable local couples which accelerate corrosion. On the other hand, the layer of oxide formed on aluminium under normal conditions is extremely tough and coherent, and prevents further corrosion when a certain small thickness has been reached. Where corrosion is more rapid the coating may be porous. The loose coating of oxide which is formed when aluminium is rubbed with mercury has no coherence. In moist, tropical countries aluminium corrodes more rapidly, and the coating, although apparently continuous, may be minutely porous. Aluminium drinking vessels in hot climates acquire a foul taste, doubtless owing to the absorptive properties of this porous coating of oxide.

With a view to examining changes in the physical condition of the metal and of the corrosion product, as well as the amount of corrosion, the writer has carried out several series of experiments, mainly in collaboration with Mr. S. Whyte, B.Sc., with alloys of copper with zinc and other metals (Desch and Whyte, *Journ. Inst. Metals*, 1913, x., 304; Whyte and Desch, *Ibid.*, 1914, xi., 235; Whyte, *Ibid.*, 1915, xiii., 80; Desch and Hyman, *Ibid.*, 1915, xiv.). Specimens of the size used for microscopical examination are corroded in a salt solution, being made the anode in a cell of 1 or 2 cc. capacity with a platinum gauze cathode. If necessary the action is hastened by the application of a small external e.m.f. A temporary containing vessel is built up of plasticine. After a determined time the contents of the cell are washed out into a beaker for analysis, and the surface of the specimen is examined. In this way a separate analysis of the products (a) to (e) may be made, the adherent deposits being removed by gentle scraping if necessary. Special colorimetric

methods of analysis are used to determine the proportions of dissolved metals, amounting in some cases only to a hundredth of a mgrm. or less, and in the continuation of the work microchemical methods are being used. The specimen is examined microscopically at each stage of the process. A convenient laboratory apparatus has been devised by means of which successive experiments may be made rapidly under exactly similar conditions (Desch, *Journ. Soc. Chem. Ind.*, 1915, xxxiv., 258; Desch and Hyman, *loc. cit.*).

When an annealed α brass, which consists of a homogeneous solid solution, is corroded under these conditions, using a 5 per cent solution of sodium chloride and an applied e.m.f. of 2 volts, the surface is attacked, zinc being dissolved much more rapidly than copper, so that a surface layer is obtained, consisting mainly of metallic copper mixed with basic salts. When the latter are removed by washing with very dilute hydrochloric acid, copper is left in very perfect octahedral crystals. It is interesting to observe that this dezincification takes place *per saltum*, there being an abrupt change from copper to unaltered brass, without any intermediate zone in which the proportion of zinc is less than that originally present, but greater than in the superficial layer. This is characteristic of the dezincification of brass, whether occurring naturally in the course of use or brought about artificially as described above. A transverse section shows this clearly. Under a higher magnification, it is seen that the dezincification proceeds along the boundaries between crystal grains, indicating that the bounding surfaces are more strongly electro-positive than the mass of the crystals. Where twinned crystals are present, as in annealed brass, the removal of zinc also proceeds along twinning planes. Both of these effects are seen in Fig. 2, where the dark, rough areas represent copper invading the brass along boundaries and twinning planes.

The spongy layer of crystalline copper offers a very large surface, and is therefore readily oxidised. This fact accounts for the presence of a bright red layer, consisting mainly of cuprous oxide, on the corroded surface of brass tubes. The oxide layer is of secondary, not primary, origin.

An unannealed cast brass is not quite homogeneous, but exhibits "coring," each crystal grain becoming richer in zinc from the centre to the periphery. Such an alloy, owing to imperfect homogeneity, is rather more rapidly corroded than annealed brass, but the difference is not large.

The homogeneous β brasses, which are in general too brittle for industrial use, are corroded in a similar manner, but more rapidly. The process is almost entirely one of dezincification, very little copper being dissolved, whilst the residual layer contains sometimes as much as 99.6 per cent of copper. The crystalline structure of the brass beneath this overlying layer is very clearly developed, and in other respects the process advances just as in the α alloys.

Alloys of the Muntz metal class have a duplex structure, being made up of the α and β solid solutions in conjunction. It was observed by Milton and Larke (J. T. Milton and W. J. Larke, *Proc. Inst. Civ. Eng.*, 1903, cliv., 138) that the corrosion of Muntz metal in sea-water proceeds in such a way that a bolt or plate may retain its form and metallic appearance perfectly, although almost devoid of strength. A transverse section shows an outer layer which is coppered in colour, and often an inner core which is yellow, but brittle and weak, whilst if the corrosion has stopped short of completion there may be a central core of unchanged metal. A similar observation had been made by Arnold (J. O. Arnold, *Engineer*, 1898, lxxxv., 363), whose explanation is confirmed by microscopical examination. The β constituent, being the more electro-positive, is first dezincified and converted into a mass of porous, crystalline copper. This stage is seen in Fig. 3, which represents an alloy of this kind after a few minutes' corrosion in the laboratory apparatus described above. The dark β areas

are replaced by copper. Only when this change has progressed to some depth does the attack spread to the α crystals, after which the removal of zinc from these proceeds to completion. The spongy copper retains the original form of the crystals, so that a perfect pseudomorph remains, showing the original arrangement under the microscope. This successive replacement of the two constituents by copper was first observed by Arnold (*loc. cit.*), who showed that the strongly electro-positive β was first attacked, and that after its conversion to copper it became electro-negative to α , and so accelerated the corrosion of the latter. When the β has been so far attacked that it has the same composition at the surface as the α , it might seem that a state of equilibrium would be reached, after which the two would be attacked equally, but in fact the great porosity of the partly corroded β causes the attack to be confined to it entirely.

Reversals of electrolytic action of this kind are sometimes very striking. When a mild steel containing manganese is corroded in the small electrolytic apparatus, the ferrite only is at first attacked, leaving the pearlite bright and in relief (Desch and Whyte, *J. W. of Scotland Iron and Steel Institute*, 1914, xxi., 176). The structure at this stage is just the reverse of that produced by etching with acids. Reversal then takes place, and at one point the whole surface is equally darkened, after which the pearlite is more rapidly attacked, and ultimately ferrite is left in relief, as in ordinary etching. The point of reversal coincides with the maximum solution of manganese, and after it is passed the ratio of manganese to iron going into solution again falls.

The effect of a second constituent in accelerating corrosion is also shown in Fig. 4. This represents a light aluminium alloy, containing about 4 per cent of copper. A eutectic of aluminium and CuAl_2 is present, but in such small quantity that a eutectic structure is rarely seen, and the compound mostly presents itself in narrow, isolated masses. When electrolytically corroded in salt solution, the compound remains unattacked, and the ground-mass, instead of dissolving uniformly over its entire surface, is pitted locally, the pits being closely related to the masses of CuAl_2 , either immediately adjoining them or following their outline at a short distance. The influence of local electrolytic couples is here obvious.

In gun-metals it is the α constituent which is first attacked, the eutectoid δ remaining in relief until the corrosion is very deep. In copper-tin $\alpha\beta$ alloys, the electrochemical difference between α and β is very small.

The protective action of certain metals when added to alloys is next to be considered. As the result of experience in the behaviour of alloys in sea-water, the Admiralty introduced the use of 1 per cent of tin in $\alpha\beta$ alloys of copper and zinc. The resulting "naval brass" is much more resistant to corrosion by sea-water than the simpler alloy. The explanation of this effect is not immediately obvious. The 1 per cent of tin enters into solid solution, and has no effect on the structure beyond slightly increasing the proportion of β , a change in itself conducive to corrosion. The lowering of the electrolytic potential of the brass by the solution of the tin is too small to have any appreciable effect. The experiments cited above have shown that the actual protective effect is in all probability purely mechanical. At first, the presence of tin very slightly accelerates corrosion, but in a neutral or slightly alkaline electrolyte a layer of basic tin salt is rapidly formed, and adheres to the surface so firmly as to form an almost impermeable varnish, which protects the metal from further action. The α brasses are similarly protected by the addition of 1 per cent of tin, the alloy 70 : 29 : 1 being in common use for condenser tubes.

Lead exerts a protective action on an α brass when present in sufficient quantity. It does not enter into solid solution, and each particle, being electro-negative, causes local dezincification in its immediate neighbourhood. With 1 per cent of lead, this appears to be the extent of

its influence, which is therefore harmful, but a larger proportion of lead gives rise to the formation of a sufficiently tough layer of basic salts. The good quality of condenser tubes containing 2 per cent of lead is thus explained.

A layer of manganese oxide may exert a protective action. Thus light aluminium alloys, one of which contained 2 per cent each of copper and manganese, and the other 3 per cent of copper and 1 per cent of manganese, became coated with a dark adherent layer when kept for 121 days in sea-water, the corrosion being much less than that of pure aluminium (W. Roserhain and F. C. A. H. Lansbury, Ninth Report to Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1910, 283).

On the other hand, basic salts which fail to form a closely adherent varnish may greatly accelerate corrosion. This is especially so with copper oxychloride. In a case investigated by the writer, some brass locomotive boiler tubes were found to be very badly pitted, especially at the fire-box end. In each pit was found a small mass of green copper oxychloride, which had served as the electro-negative part of a local couple. The coal used in the locomotive proved to have been repeatedly drenched with sea-water, so that chlorine and hydrogen chloride were formed during its combustion.

The formation of local couples may also be brought about by the adhesion of loose particles of a substance electro-negative to the metal being corroded. It is generally considered that particles of coke often play this part in the corrosion of condenser tubes. This has been disputed in the valuable Second Report to the Corrosion Committee of the Institute of Metals (G. D. Bengough and R. M. Jones, *Journ. Inst. Metals*, 1913, x., 13; for the First Report, see G. D. Bengough, *Ibid.*, 1912, vii., 51), but recent experiments seem to establish it (A. Philip, *Ibid.*, 1914, xii., 133). Such an effect is in accordance with the general behaviour of electro-negative particles.

It is believed that the method of study of corrosion outlined in the present paper, by taking into account the mechanical and physical factors involved in the process, makes it possible to investigate, with more precision than is possible in the ordinary methods of testing, the mechanism of the process, and it is for this reason that an account of the preliminary results is laid before the Society.

THE RELATIVE CORRODIBILITIES OF IRON AND STEEL.*

By J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.

EVER since the discovery of iron man must have been aware of the corrosion of that metal upon exposure to moist air. In the ruins of the ancient Swiss lake villages iron protected by brass or bronze has been found (Bennett H. Brough, *Journ. Iron Steel Inst.*, 1906, i., 233), showing that the early metallurgists sought to prepare articles combining the strength of iron with the incorrodibility of bronze. In our local museum at Worcester are exhibited bells similar to the Swiss cow-bells, presumably of Roman origin, and which consist of iron coated with brass or bronze. Pliny, writing nearly 2000 years ago, draws attention to the fact that not only will iron rust, but that some ores yield a metal "which is more particularly liable to rust," thus showing the dawn, even at that early date, of an appreciation of quantitative corrodibility (see Pliny, Book xxxiv., c. 41).

In Pliny's day, and, indeed, for many centuries later, only a very limited variety of manufactured irons was known, namely, those produced by direct reduction of different ores. At the present time, however, we have to deal with an almost endless series of wrought-irons, cast-irons, and steels, with the result that the problems of cor-

* A Contribution to a General Discussion on "The Corrosion of Metals" held before the Faraday Society, December 8, 1915.

rosion are each year becoming increasingly numerous and perplexing.

The problem of corrosion is one of the most important that the iron and steel trade has to face. From the economic point of view—and this is a point of peculiar importance at the present crisis—vast possibilities lie in the wake of a correct understanding of the causes leading to corrosion and the best methods of counteracting them. A question which is generally exercising the minds of both customers and manufacturers is "Which is the more corrodible, iron or steel?" It is with the hope of being able to throw a little light upon this much debated problem that I am venturing to address you to-night.

Different kinds of Corrosion.

Before dealing directly with the relative corrodibilities of iron and steel, it is desirable to explain exactly what is meant by corrosion. The term is used somewhat widely, but generally speaking may be taken to indicate the solution or oxidation of the pure metal or its constituents. For the sake of convenience three main types of corrosion may be distinguished. These are not to be regarded as isolated and independent; rather are they extreme cases of an almost infinite variety of reactions, dependent upon the composition of the metal and the nature of the corroding influences.

1. *Solution in Acid.*—When immersed in aqueous solutions of many acids, such as sulphuric or hydrochloric, iron readily dissolves, yielding ferrous salts. If the acid is fairly concentrated (0.5 per cent sulphuric acid solution is very suitable), and always present in sufficient excess, the surface of the metal remains relatively bright, and no precipitation of rust takes place. Were it not for the continuous evolution of bubbles of hydrogen gas there would often be little to indicate that the iron is being attacked. If, however, the iron is weighed before and after exposure to the acid the loss in weight occurring may be taken as a measure either of the corrosivity of the liquid or of the corrodibility of the metal.

This is the principle of the so-called acceleration tests, it being assumed that the rate of solution in the acid is a measure of the resistance the metal would offer to corrosion in neutral media—a pernicious supposition contrary to theory and practice alike (see Friend, "The Corrosion of Iron and Steel," 1911, 273). We shall have occasion to refer to this point again in the sequel.

2. *Graphitisation.*—This is a form of corrosion to which cast-iron is particularly liable, the mass becoming so soft as to be readily cut with a knife. The metallic portion is more or less completely oxidised, mainly to ferrous oxide, some of which has frequently been washed away, the remainder collecting within the pores of the now isolated mass of graphite (Berzelius, "Traité de Chimie," 1831, iii.; Rennie, *Min. Proc. Inst. Civil Eng.*, 1845, iv., 323; Draper, *CHEMICAL NEWS*, 1887, lvi., 251; Kröhnke, *Metallurgie*, 1910, vii., 674; Le Naour, *Journ Iron Steel Inst.*, 1893, i., 526 (abstract); Holgate, *Gas World*, 1913, lvi., 479; Krizian, *Zeit. öffentliche Chem.*, 1912, xviii., 433). This reaction does not usually take place with the purer forms of iron, although a few cases of similar softening are on record where wrought-iron has been subjected to prolonged immersion in sea-water (Mallet, *British Assoc. Reports*, 1838, p. 259; Lidy, *Engineering News*, 1897, xxxix., 85). The percentage of carbon is, in such cases, of course, much less than with cast-iron, but is frequently much higher than the normal in consequence of the solution and removal of some of the iron.

3. *Formation of Rust.*—The most usual form of corrosion is that in which the iron is oxidised more or less completely to brown hydrated ferric oxide, which remains *in situ*, and is popularly known as rust.

When relatively pure iron is suspended in tap-water the ensuing rust consists almost entirely of hydrated ferric oxide, and there is usually no pitting. If, on the other hand, the metal is allowed to become alternately wet and

dry, both ferrous and ferric oxides are produced, the proportion of the former varying enormously according to circumstances. In this case pitting is frequent.

When iron is only partially immersed in water, the corrosion just at the surface of the latter is particularly severe, and the resulting mass of rust is usually high in ferrous oxide. Complete immersion of iron in concentrated solutions of nitrates of the alkali metals may be made to yield a deep green oxide, whilst a dilute solution of oxalic acid develops a beautiful lemon-yellow form of rust. Dilute phosphate solutions may yield a white rust, whilst alkaline iodides can be made to yield black rust.

Pitting can easily be induced by total immersion in dilute solutions of mineral salts rendered very faintly alkaline by the addition of caustic potash (Friend, *Science Progress*, 1913, v., 202). In such cases the rust invariably contains relatively large quantities of ferrous oxide, in addition to the brown ferric oxide, and the pitting probably occurs at points where slight traces of impurity are present in the metal. Even Kahlbaum's pure iron foil, prepared electrolytically, readily pits in these circumstances, a fact which proves that certain corroding media are specially liable to induce pitting, since immersion in tap-water or solutions of the majority of inorganic salts merely causes the foil to rust evenly over its entire surface. This fact is one of extreme importance, illustrating the need for investigating the corroding media as well as the metal.

Factors Involved in a Determination of the Relative Corrodibilities of Iron and Steel.

It cannot be too strongly emphasised that the task of satisfactorily determining the relative corrodibilities of iron and steel is one of immense difficulty in view of the numerous factors involved. The five most important of these are as follows:—

1. *The Selection of truly representative Samples of Metal.*—There can be no doubt that many of the incongruities of earlier researches arose from the fact that some investigators worked with poor steel and good wrought iron, thereby obtaining results favourable to the latter; whilst others examined good steels and poor irons, thus obtaining diametrically opposite results. It must be obvious that the two classes of metal can only be properly compared when thoroughly representative samples of each are dealt with. Since the metals are made in such a variety of ways and with such varying chemical compositions it is essential that a very large number of samples be taken. This is where the majority of the researches are at fault, with the result that the conclusions, although excellent for the field they cover, are not based upon sufficient data to render them of very great practical value.

2. *The Standard of Corrodibility to be adopted.*—Practically all the earlier researches were based upon the loss in weight undergone by the metals when the rust produced by varying corroding media had been removed—a method that is adopted very largely at the present time. In the absence of pitting the results are thoroughly trustworthy and of great value. But, as has been pointed out, certain kinds of corroding media favour the development of serious pitting, and in these cases the mere determination of total superficial loss in weight may not prove particularly helpful. For example, it is conceivable that an iron boiler might lose several pounds in weight through uniform superficial corrosion and yet not be much the worse. On the other hand, a single ounce removed through pitting might be sufficient to perforate the metal and lead to disastrous consequences. In such cases a determination of the depth of pitting is of the utmost importance, and, as will be seen later, this has been realised by several recent investigators. In the case of bars of iron, Heathcote suggests that determination of the tensile strengths after corrosion would give a measure of the depth of pitting, and this combined with weighing tests should be very valuable.

Another point to bear in mind is that corrosion tests

should not in general be carried out to destruction. In practice ironwork usually becomes unsafe long before it is "destroyed" from a corrosion point of view, and the severity with which corrosion tests are carried out should depend upon the stage at which the metals are to be discarded in practice.

3. *The Corroding Media to be Employed.*—No one type of metal must be expected to resist equally well all kinds of corroding media. Some are particularly resistant to acid attack, whilst others withstand the action of fumes easily. Yet a third metal will prove most suitable for resisting neutral corroding agencies, such as river water or fresh air, whilst a fourth excels in its resistance to the effects of sea-water. These points are strikingly well illustrated by the following data:—

(a) Two steels examined by the writer yielded almost identical corrosion factors when exposed to various neutral influences, but in 0.5 per cent sulphuric acid the second steel corroded two and a-half times as rapidly as the first (Friend, Bentley, and West, *Journ. Iron Steel Inst.*, 1912, i., 249; 1913, i., 383; this variation in acid corroding media was probably due to the fact that Steel 2 had a higher manganese content—0.685 per cent—than Steel 1—0.39 per cent).

	Corrosion factors in—				
	Water.	Wet and dry.	Hot and cold water.	Sea-water.	0.5 per cent H ₂ SO ₄ .
Steel 1	100	100	100	100	100
Steel 2	108	100	100	105	259

(b) In 1907 Fraser (*Journ. West Scotland Iron Steel Inst.*, 1907, xiv., 82) observed an analogous discrepancy in the behaviour of acid and basic steels of very similar compositions.

Corroding medium.	Corrosion factors of—	
	Basic steel.	Acid steel.
Air	100	101
River-water	100	101
Rock-salt solution	100	90
Common salt solution	100	106
Sulphuric acid (7.5 per cent) ..	100	306

These, together with the previous results, illustrate very clearly the misleading nature of acceleration tests.

(c) Rudeloff (see the tables given later), in 1902, found that, by exposing different samples of iron and steel to smelting furnace gases, his wrought-iron plates had the decided advantage, whereas in the tests conducted with air and with ditch-water as corroding media there was much less to choose between the two metals.

From these and numerous other published data it is evident that the nature of the corroding medium must be known before a reliable opinion can be expressed as to the best metal to resist the same.

4. *The Composition of the Metal.*—Steels offer a very wide range for variation of composition, but for present purposes all "special" steels may be eliminated. We are only concerned with those more common types that are used for such purposes as will bear commercial competition with wrought iron. The main chemical differences are thus confined to variations in the carbon and manganese contents. At the present time the influence exerted by these two elements, both singly and together, upon the corrodibility of iron has not been thoroughly investigated. An extensive research on this problem is being carried out by Sir Robert Hadfield and the writer, and although it is too early yet to discuss the results in detail, it may be mentioned that small variations in the manganese content of the metal have been observed to influence, to a hitherto unsuspected extent, the resistance towards corroding media.

Silicon, phosphorus, and sulphur are usually kept fairly low because small increases in their amounts may lead to pronounced alterations in the physical properties of the

metal, which would prove awkward in practice. If a given sample of steel happens to possess abnormally high percentages of any or all of these elements it is either due to accidental circumstances or to meet the special requirements of the customer. In either case the metal falls out of discussion in the present paper.

5. *The Homogeneity and Physical Condition of the Metal.*—Steel is, from the nature of its manufacture, particularly liable to segregation and to variation in its physical condition. It was probably on account of this that the earlier wrought irons frequently had the advantage over the steels. But modern improvements in the manufacture of the two metals have tended to minimise these differences, although the last named have not as yet disappeared and probably never will completely disappear.

(To be continued).

NOTICES OF BOOKS.

A Text-book of Inorganic Chemistry. Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C. Vol. VIII. *The Halogens and their Alloys.* By GEOFFREY MARTIN, D.Sc. (Lond. and Bristol), Ph.D. (Rostock), and E. A. DANCASIER, B.Sc. (Lond.). London: Charles Griffin and Co., Ltd. 1915.

THIS volume of the treatise on inorganic chemistry, which is in course of issue under the editorship of Dr. J. Newton Friend, gives an account of the properties and preparation of the elements of the seventh group of the Periodic Table, including the halogens and manganese and their principal compounds. A very great many references to original papers and to other standard works in various languages are given, and numbers of tables of physical and other data. Manufacturing processes are treated briefly only, the book being primarily a text-book of pure chemistry; in some respects the authors have not been very wise in their selection of the technical subjects for treatment, thus in view of the very rapidly increasing importance of electrolytic methods of preparing chlorine fuller details of the process would probably have been appreciated. Methods of detection and estimation are included, and brief accounts of the uses to which some of the substances are put.

Resolution of Planck's Constant and Rydberg's Constant, and the Origin and Inter-relations of Spectra Series. By JAS. STEWART. Paisley: J. and R. Parlange. 1915.

THIS pamphlet gives the conclusions which the author has drawn from his study of Bohr's work on the nature of line spectra. He claims to have established by reasoning from dynamical formulæ simple values of Planck's and Rydberg's constants, the only physical constant involved in the value of the latter being the velocity of light. Some general conclusions concerning the origin and inter-relation of spectral series are also discussed, and it is possible that the author's views may suggest to other workers some useful lines of research on the structure of the atom.

A Student's Book on Soils and Manures. By E. J. RUSSELL, D.Sc. Cambridge: The University Press. 1915.

THIS manual for students in farming institutes could also with advantage be studied by the practical man who wishes to increase his knowledge of the scientific basis of agriculture. The author writes with the high aim of helping the farmer to make the most out of his work—to draw the benefits of increased interest and intellectual

appreciation as well as those of material success, and he has produced a book which is well suited for the education of the new generation of agricultural students, upon whose activity and knowledge so much depends. In the first part of the book an account is given of the soil in its natural state; the requirements of plants are first discussed, and the composition of the soil, and some account is given of the organic matter of the soil, and the effect of climate upon fertility. The farmer's methods of controlling the soil and getting the most out of it are treated in Part II., while the third part deals with the nature and use of fertilisers. Some attention is paid to the valuation of manures, and the composition and properties of all the common manures at the disposal of the British farmer are briefly described.

Biology. By GARY N. CALKINS, Ph.D. New York: Henry Holt and Company.

THIS text-book of biology is based upon Sedgwick and Wilson's course of General Biology, which is much used in America, and will be found useful by students working for intermediate examinations in science. Organisms of one cell, organisms of tissues, and organisms of organs are considered in succession, and an interesting chapter is provided on the origin and perpetuation of variations and on modern principles of heredity. The book would be most appreciated by students who had already been through a school course of biology, though no previous knowledge of the subject is actually essential.

CORRESPONDENCE.

PREPARATION OF SULPHURETTED HYDROGEN.

To the Editor of the Chemical News.

SIR,—I was entirely unaware of the article in the CHEMICAL NEWS of May 3, 1907, referred to by Mr. Southerden in your issue of December 17, 1915, when I wrote the description appearing in the CHEMICAL NEWS of November 19, 1915.

I regret the seeming plagiarism, and if Mr. Southerden thinks the support for the reagent which I devised is any improvement on a chipped stopper he is quite welcome to adopt the idea.—I am, &c.,

H. ELLIS.

Chemical Laboratory, Leeds Forge, Leeds,
January 11, 1916.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

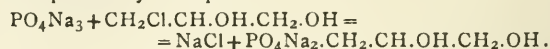
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 22, November 29, 1915.

Atomic Weight of Cadmium.—Echsner de Coninck and M. Gérard.—The authors purified the metal by dissolving it in sulphuric acid and passing a current of H_2S through the solution for some hours; thus the cadmium was precipitated with copper and a small amount of zinc. The precipitate was washed and dissolved in concentrated HCl. The excess of acid was removed by evaporation, and a large excess of a concentrated solution of ammonium carbonate was added. Thus only the cadmium carbonate

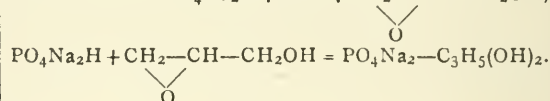
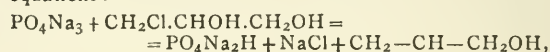
was precipitated. It was washed, dried, and weighed, and reduced in a current of pure hydrogen. If p is the weight of the $CdCO_3$ and p' that of the Cd, the atomic weight is given by the equation $\frac{p}{p'} = \frac{x+60}{x}$. The mean of five

determinations was found to be 112.32, while the value adopted by the International Commission is 112.40.

Mechanism of Action of Tribasic Sodium Phosphate on Monochlorhydrine of Glycerin.—O. Bailly.—King and Pyman have recently shown that the action of tribasic sodium phosphate on glycerin α -monochlorhydrine in cold aqueous solution gives sodium glycero-phosphate, and imagine that the mechanism of the reaction is expressed by the equation—



The author finds, however, that the liquid becomes appreciably acid during the reaction, and he concludes that some disodium phosphate is formed. He believes that the true reaction is expressed by the following equations:—



No. 23, December 6, 1915.

Series of Hydroxo-pentamino-platinic Salts.—L. Tschugaeff and W. Khlopine.—The carbonate of the hydroxo-pentamino-platinic series may be prepared by the action of ozone on Peyrone's chloride, $(NH_3)_2PtCl_2$, in presence of ammonium carbonate and ammonia in excess. The general formula of the new series is $[Pt_5NH_3OH]X_2$, where X is Cl, NO_3 , &c. The salts of the series are analogous to those of the series $[Pt_5NH_3Cl]X_3$ and of $[Pt_6NH_3]X_4$, and also to the salts of barium. Both pentamino-platinic series correspond to strong bases; they are characterised by the insolubility of their carbonates and sulphates in pure water and the solubility of these salts in fixed alkalis.

MEETINGS FOR THE WEEK.

TUESDAY, 25th.—Royal Institution, 3. "The Physiology of Anger and Fear," by Prof. C. S. Sherrington.

WEDNESDAY, 26th.—Royal Society of Arts, 4.30. "The Effect of the War on Cotton Growing in the British Empire," by J. Arthur Hutton.

THURSDAY, 27th.—Royal Institution, 3. "The Utilisation of Energy from Coal—The Chemistry and Economics of Coal and its By-products," by Prof. W. A. Bone. Royal Society. "The Theory of the Helmholtz Resonator," by Lord Rayleigh. "A Collision Predictor," by J. Joly. "Discussion of New Magnetic Data, especially the Diurnal Irregularities of Horizontal Force and Vertical Force, from Ordinary Days of the eleven years 1890 to 1900," by C. Chree. "Portable Variometer for Magnetic Surveying," by G. W. Walker. "The Single Line Spectrum of Magnesium and other Metals and their Ionising Potentials," by J. C. McLennan. "Microscopic Structure of Semi-permeable Membranes, and the Part Played by Surface Forces in Osmosis," by F. Tinker. "The Reduction of Metallic Oxides with Hydrogen at High Pressures," by E. Newbery and J. N. Firing. "Discontinuous Fluid Motion past a Curved Boundary," by H. Levy.

FRIDAY, 28th.—Royal Institution, 5.30. "The Science of Clothing and the Prevention of Trench Feet," by Dr. Leonard Hill.

Physical, 5. (Guthrie Lecture). "Some Problems of Living Matter," by W. B. Hardy.

SATURDAY, 29th.—Royal Institution, 3. "Raphael and Michael Angelo," by C. J. Holmes.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2931.

THE PURIFICATION OF TRINITROTOLUENE.

By MAURICE COPISAROW, M.Sc.,
Honorary Research Fellow, Chemical Department, The University,
Manchester.

As indicated in a previous paper (CHEMICAL NEWS, 1915, cxii., 247) the manufacture of trinitrotoluene, simple as it may appear, is not too simple, and unless care is taken side-reactions may set in greatly affecting the quality and yield of the desired product.

A closer study reveals the fact that the difficulties are not confined to the nitrating plant alone, but are also met with in the subsequent process of purification. The method of purification must vary according to the initial state of purity of the crude product.

The purification of a charge successfully nitrated is fairly simple.

Mineral matter, intermediate and by-products, being present only in very small quantities the purification is limited to the removal of the acid and volatile matter (moisture) from the crude trinitrotoluene.

The acid can be removed by agitating the molten trinitrotoluene with hot water several times. On letting the washings cool the dissolved portion of T.N.T. crystallises in fine needles.

It is not advisable to heat the molten T.N.T. in water too long; firstly, as it is somewhat volatile in steam (hence the bitter taste of the water-vapour observed in the washing department; the vapour may cause headaches and even sickness), and, secondly, a side reaction may set in with the formation of dinitro-cresols in a manner similar to the formation of dinitrohydroxybenzoic acids from trinitrobenzoic acids (Körner and Contardi¹, Giua²).

The use of alkalis for the neutralisation of the acid is not permissible as they react readily with T.N.T. (CHEMICAL NEWS, 1915, cxii., 283). The use of sodium bicarbonate is superfluous in the cold and injurious in the hot. Under proper conditions of supervision and technical arrangement water is the safest and most efficient medium for the removal of the acid. The advocates of the sodium bicarbonate treatment must consider, besides its effect on T.N.T., the possibility of the formation of sodium salts of the acid and phenolic by-products, salts not too soluble and certainly more dangerous than the by-products themselves.

The volatile matter (moisture) can be removed by keeping the T.N.T. several hours at 95–100° C.

The purification of a crude product containing a comparatively high percentage of mineral matter and organic by-products is a somewhat more complicated problem.

The most radical way in such a case is to re-crystallise the crude product from alcohol or toluene (in the latter case the mother-liquor from the crystallisation can be transferred directly to the nitrating plant), thus removing practically all impurities. But owing to plant considerations this method is not always the most available.

The second method consists in treating the crude product with (1) sulphuric acid; (2) nitric acid; or (3) sulphuric acid with the addition of about 5 per cent of nitric acid (acid as such or sodium nitrate). The use of sulphuric acid is based on the fact that trinitrotoluene is not easily attacked by concentrated sulphuric acid, in which it is fairly soluble at 90–100°, separating unchanged on cooling or dilution, whilst most of the impurities are sulphonated.

The advantage of adding a little nitric acid to the sulphuric* consists in the prevention of a reversible reaction

* The sulphuric acid employed need not be the very concentrated acid of 1·65 and upwards specific gravity will serve the purpose.

taking place; e.g., the substitution of nitro- by sulpho-groups in the T.N.T., and the partial oxidation of the organic impurities.

In case sulphuric acid is used for the purification it is not advisable to lower the specific gravity on dilution beyond 1·2, as:—

(1) A fairly high concentration prevents some of the organic impurities from separating out with the trinitrotoluene.

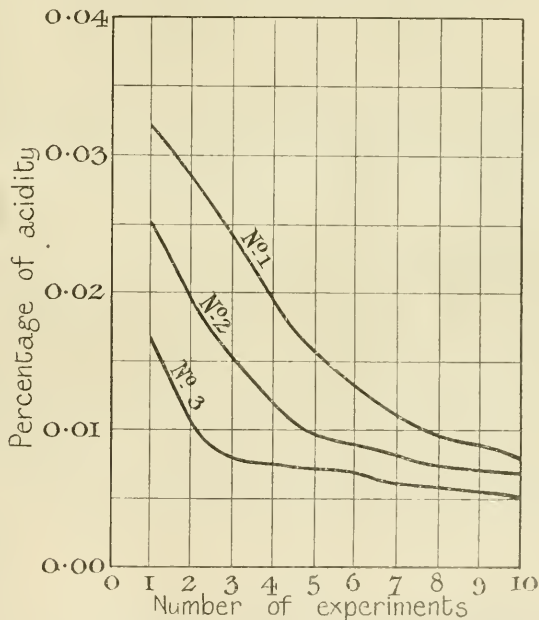
(2) It makes easier the subsequent re-use or concentration of the acid.

(3) The solubility of trinitrotoluene in acid does not decrease on further dilution (McHutchison and Wright³).

The acidity of crude trinitrotoluene presents some interesting points.

The assumption of the acidity of crude trinitrotoluene as being due to sulphuric acid, whilst correct to all intents and purposes in case of the crude product direct from the nitrating plant, is contradicted in case of properly washed T.N.T. by the following facts:—

(1) Two samples of crude T.N.T. varying in purity (as indicated by their respective setting-points and colour) vary also in their acidity, though both washed in an



identical manner, the less pure indicating invariably a higher acidity.

(2) One or two extractions of properly washed T.N.T. are quite inadequate either to indicate the true acidity or to free the product from acid.

(3) The aqueous extract of well-washed crude T.N.T., whilst showing distinct acidity, as indicated on titrating with caustic soda (phenolphthalein as an indicator), does not give any indication of turbidity, when mixed with a solution of barium chloride (sulphuric acid present in a solution in proportion 1:200000 is easily detected), and does not affect litmus or congo-red.

To determine the rate of change of acidity with the number of extractions, to which crude T.N.T. is subjected, the following experiments were carried out.

Three samples of crude properly washed T.N.T. taken from different batches were each treated in the following manner:—

20 grms. of powdered T.N.T. were treated with 100 cc. of boiling distilled water, the molten T.N.T. vigorously agitated with a glass rod, the mixture cooled to about

16–17° C., the water extract run off carefully into a small flask, and titrated with N/20 NaOH using phenolphthalein as an indicator.

The remaining T.N.T. was again extracted with hot water, cooled, and titrated; the operation being repeated ten times for each sample. The following results were obtained, the acidity being calculated as sulphuric acid.*

	Samples.		
	No. 1. Dark brown.	No. 2. Yellowish brown.	No. 3. Orange- yellow.
Setting-points (a) ..	73° 6' C.	75° 4' C.	76° 0' C.
1. Acidity (per cent)	0·0320	0·0250	0·0165
2. " "	0·0280	0·0190	0·0100
3. " "	0·0240	0·0150	0·0080
4. " "	0·0190	0·0120	0·0075
5. " "	0·0160	0·0095	0·0075
6. " "	0·0130	0·0090	0·0070
7. " "	0·0110	0·0080	0·0060
8. " "	0·0095	0·0075	0·0060
9. " "	0·0090	0·0070	0·0055
10. " "	0·0080	0·0070	0·0050
	0·0695	0·0190	0·0790

(a) The setting-points were taken of portions heated three hours in a steam-oven. No such heating was applied to portions reserved for the acidity test.

Even pure α -trinitrotoluene (re-crystallised from acetone and then from alcohol) melting at 80·7° C. was found to be not quite neutral, and on extracting it in a manner described above had acidities varying between 0·0025 per cent and 0·0050 per cent, calculated as sulphuric acid.

Representing the results obtained above in a graphic form we get the curves shown in the accompanying diagram.

The persistency of the acidity of crude T.N.T. and the general dependence of the acidity upon the purity of the product would suggest that the acidity of well-washed crude T.N.T. is due not to the retaining of any mineral acid, but to the contamination with organic acid or phenolic by-products.

There is more reason to attribute the acidity to phenolic than acid bodies, as the latter are far more soluble in hot water, and are removed to a great extent during the washing.

Whilst the acidity of re-crystallised T.N.T. could be attributed to the formation of nitroic acids or dinitro-cresols under the influence of the hot water, the comparatively high acidity of washed crude T.N.T. must be attributed to the by-products formed during the nitration.

References.

1. *Atti R. Accad. Lincei*, 1914, (v.), xxiii., II., 464.
2. *Ibid.*, 484; *Gazetta*, 1915, xlv., 345, 352.
3. *Journ. Soc. Chem. Ind.*, 1915, xxxiv., 781.

Royal Society of Arts.—*Albert Medal*.—In the absence of the President of the Society, H.R.H. the Duke of Connaught and Strathearn, K.G., Dr. Dugald Clerk, F.R.S., Chairman of the Council, at a meeting of the Council on January 24, presented the Society's Albert Medal to Prof. Sir Joseph John Thomson, O.M., D.Sc., LL.D., F.R.S., "for his researches in chemistry and physics, and their application to the advancement of Arts, Manufactures, and Commerce." The Society's Albert Medal was founded in 1863 as a memorial of H.R.H., the Prince Consort, and is awarded annually "for distinguished merit in promoting Arts, Manufactures, and Commerce."

* The gradual decrease of the acidity values will become slightly smaller on the introduction of a correction for the solubility of T.N.T. in water (0·021 per cent at 15° C.; 0·164 per cent at 100° C.).

THE RELATIVE CORRODIBILITIES OF IRON AND STEEL.*

By J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.

(Concluded from p. 35).

Results of Experiment and Experience.

FROM the foregoing it is evident that our problem is by no means as simple as might appear at the first glance. The factors involved are too numerous to allow of the subject being summarily dismissed in favour either of iron or of steel as the result of a few isolated laboratory experiments, and whilst theoretical considerations may give us a general idea as to the type of metal that may be expected to withstand corroding media most successfully, there can be no doubt that the final appeal must always be made to the results of experience and of experiments carried out with a liberal hand on a large scale under actual working conditions.

More work has been carried out along these lines than the average reader is aware, and the following brief summary of the more important researches may prove useful:—

1. One of the earliest researches carried out on a large scale is that of William Parker (*Journ. Iron and Steel Inst.*, 1881, i., 39), who in 1881 exposed plates of seven different kinds of wrought iron and of four varieties of steel to various corroding influences—namely, London air, sea-water, bilge-water, and boiler-water. The results obtained were distinctly in favour of wrought iron, the mean results for the relative losses in weight consequent upon corrosion being—

Wrought iron	100
Steel	133

The results, however, are now of historic interest rather than of practical value, for the simple reason that since 1881 the different processes for the manufacture of both iron and steel have been more or less completely revolutionised.

2. The researches of Rudeloff, published in 1902 (*Mitteilungen aus dem königlichen technischen Versuchsanstalten*, Berlin, 1902, xx., 83) must be placed in a different category, and are worthy of careful consideration. (The tables are compiled and calculated from tables 48 and 49, p. 176 of Rudeloff's memoir). Unfortunately the

Metal.	Thickness of plate. Cm.	Dry air.	Weather.	Smoke.	Ditch water.	Sea water.
Wroughtiron	0·5	100	100	100	100	100
Wroughtiron	"	200	250	0	150	158
				Mean..	..	100
Thomassteel	"	200	207	100	75	193
Basic open - hearth steel	"	200	207	100	175	193
				Mean..	..	131
Wroughtiron	0·075	100	100	100	100	100
Wroughtiron	"	146	89	100	84	82
				Mean..	..	100
Thomas steel	"	58	129	200	68	96
Basic open - hearth steel	"	125	79	100	94	113
				Mean..	..	106

* A Contribution to a General Discussion on "The Corrosion of Metals" held before the Faraday Society, December 8, 1915.

analyses of the different metals do not appear to be given, and it is therefore impossible to ascertain to what extent any variation in chemical composition may be responsible for the observed differences in corrodibility. Two sets of experiments were carried out, namely, with plates 0.5 cm. and 0.075 cm. in thickness respectively (see Table, preceding column).

Examination of the above tables reveals very considerable differences in the relative corrodibilities of the four metals in different media. The thinner plates exhibit on the whole a greater uniformity than the thicker ones; nevertheless, to take the extreme case among the former, the Thomas steel was found to corrode in smoke twice as rapidly as the other metals.

It will also be observed that the thinner steels differed among themselves quite as much as from the corresponding wrought iron standard.

Finally, it is interesting to note that there was little to choose between the mean corrodibilities of iron and steel in the case of the thinner plates, but the wrought iron had the advantage in the thicker plates.

By exposing the metals to blast-furnace gases, however, the wrought iron plates showed to an overwhelmingly great advantage. The results were as follows:—

	Plates, 0.5 cm. thick.	Plates, 0.075 cm. thick.	Mean.
Wrought iron.. ..	100	100	100
Wrought iron.. ..	0	67	
Thomas steel.. ..	600	183	500
Basic open-hearth steel.	300	250	

3. Howe and Stoughton (*Proc. Am Soc. Testing Materials*, 1908, viii., 247) in 1908 gave the results of exposing samples of American iron and steel to various corroding media. They may be tabulated as follows:—

	Weather (2 years).	River water (2 years).	Sea water (2 years).	Mean.	Weather (8 years).
Wrought iron ..	100	100	100	100	100
Steel ..	103	94	117	105	133

Consideration of the above table shows that there is little difference between the corrodibilities of the iron and steel as exhibited in the tests of two years' duration. It is interesting to note, however, that the steel shows to less advantage when the tests are prolonged to eight years, the corrosion factor for the steel being then 133, which, curiously enough, is the same as the mean value found by Parker (*vide supra*).

The authors point out, however, that mere loss in weight is not the only point to be considered in determining the relative corrodibilities of different metals. Of equal importance is the study of the pitting, because "if there is a hole the water will run out, no matter how much the pipe weighs." Plates of wrought iron and steel were therefore exposed to the action of hot aerated artificial seawater, and the depths of the pits produced were carefully measured with the following results:—

	Mean depths of deepest pits.	Relative corrodibilities.
Wrought iron	0.028 inch (mean of 9 plates)	100
Steel	0.017 inch (mean of 12 plates)	61

Here the steel has the distinct advantage, so that from this point of view the relative corrodibilities of the metals are inverted.

Howe and Stoughton also gave the results of an examination of twenty-nine pipes used in the signal systems of an American railroad, twelve of which pipes were steel and seventeen iron. Nineteen of these were practically destroyed by corrosion and pitting, the average life of the pipes being as follows:—

	Number of pipes.	Average life.	Relative corrodibilities.
Iron ..	8	10.4 years	100
Steel ..	11	13.5 years	77

Here, again, the steel has the decided advantage.

Ira Woolson in 1910 (*Engineering News*, Dec., 1910) reported on eighty-nine samples of pipes from hot-water systems in New York; seventeen of these pipes were of wrought iron, the remainder being steel. No appreciable difference in corrosion was observed.

The succeeding year J. J. Wilson reported on an investigation carried out on the Cresson Coal Field, U.S.A., to the effect that the mean depth of pitting in twenty samples of wrought-iron that had seen good service was 0.094 inch, whilst that observed for an equal number of steel samples was 0.093 inch. Here, again, the two metals appeared equally good.

In 1912 W. H. Walker (*Journ. New England Water Works Assoc.*, 1912, xxvi., No. 1) gave the results of a similar study of iron and steel service pipes, which had been in constant use throughout New England. As the pipes had not been weighed previous to insertion in the water systems, their corrodibilities could obviously not be determined by weighing. The scale and rust were removed and measurements made of the depths of pitting. As the result of sixty-four comparisons it was found that—

Iron corroded more than steel	20 cases
Steel corroded more than iron	18 "
Steel and iron equally corroded	9 "
Corrosion negligible	17 "

On the whole therefore there was no difference between the two metals.

The results of several other other researches have been published from time to time, but they all bear a similar interpretation.

As a matter of historic interest it may be mentioned that in 1881 the engineers-surveyors of Lloyd's Register possessed no fewer than 1100 marine steel boilers in actual service, and it was impossible to say which were the more satisfactory, the iron boilers or the steel ones. Even when a boiler of steel was worked alongside of one of iron in the same vessel, no material difference appeared to exist.

Howe ("The Metallurgy of Steel," 2nd ed., i., 101) mentioned in 1891 that he communicated with the leading British and American shipbuilders, &c., with a view to finding out their experience as to the relative corrodibility of iron and steel. The opinions received were almost equally divided between the two metals, and may be stated as follows:—

Steel more corrodible than iron	7 firms
Steel less corrodible than iron	8 "
No difference between steel and iron ..	14 "
Uncertain	8 "

Conclusion.

A study of the preceding data reveals the interesting fact that, whilst the mean result of examining a large number of samples of iron and steel after exposure to corroding influences indicates that the two metals are practically equally resistant, yet a very wide divergence exists between the different irons and steels in individual cases.

This is not necessarily due to any irregularity in the metals themselves, as one might be tempted to imagine, but in the majority of cases is attributable to the fact that no one metal can be expected to offer an equal resistance to all types of corroding media.

Our task, therefore, resolves itself into a wider problem, not so much as to whether iron is better than steel or *vice versa*, but rather, *Which is the best variety of iron or of steel for any particular purpose?* It is conceivable that certain makes of wrought iron will prove most useful in certain circumstances, whilst under other conditions the palm will have to be given to steel.

THE CORROSION OF A SOLID SOLUTION—
70/30 BRASS.*

By WILLIAM E. GIBBS.

WHEN an alloy of copper and zinc is immersed in sea-water it may corrode uniformly in three ways:—

(a) It may lose both constituents simultaneously and at the same rate. Both copper and zinc are then found in the corrosion product and in the proportions in which they are present in the original alloy. This is called "complete" corrosion.

(b) It may lose one constituent only, either copper or zinc. The corrosion product will then contain copper or zinc—not both. This is called "selective" corrosion.

(c) It may lose both constituents simultaneously but at different rates. The corrosion product will then contain both copper and zinc, but in a ratio which is different from that in which they occur in the alloy.

In addition to these three types of uniform corrosion localised action may occur at various points of the metal surface. This localised action may be "complete" or "selective." If the first, it produces a pit; if the second, it produces spongy copper or an alloy richer in zinc. Very frequently in practice these products of a selective local attack are worn away mechanically, and the final result is, as in the case of "complete" localised corrosion, the formation of a pit.

Some of the many factors which determine the character of a corrosive attack are:—

- The composition of the alloy.
- The temperature.
- Aeration of the sea-water.
- The concentration of the sea-water.
- The catalytic action of oxysalts of zinc and copper.
- The physical condition of the metal.
- Contact with electro negative substances, such as carbon.

(a) *The Composition of the Metal.*—The rate of corrosion of copper in sea-water at ordinary temperatures is diminished by alloying it with zinc. This diminution increases rapidly as the proportion of zinc is increased until it reaches a minimum, when the alloy contains an equal number of atoms of copper and zinc. Indeed, the alloy containing 50 atoms per cent of copper and zinc appears to be almost unattacked by sea-water at ordinary temperatures.

When the alloy contains more copper than zinc, the proportion of copper in the corrosion product is rather more than in the alloy—i.e., the copper dissolves more rapidly than the zinc. It would seem that the rate of corrosion of pure zinc is diminished by the addition of copper in a correspondingly regular manner until it reaches a minimum of the alloy containing 50 atoms per cent of zinc. In alloys containing more than this amount of zinc the zinc dissolves rather more rapidly than the copper.

The curve showing the relation between the rate of corrosion and the composition of the alloy exhibits during the first few weeks a second minimum point in the neighbourhood of the 70/30 alloy. This, however, speedily disappears, and after ten weeks the curve exhibits the familiar deep U shape, characteristic of the properties of a series of solid solutions. This curve is being re-determined by Mr. F. G. Martin and the author. It is proposed also to extend the investigation to higher temperatures. Loss of weight measurements are being supplemented by a careful analysis of the corrosion products.

(b) *The Temperature.*—The initial rate of corrosion of 70/30 brass increases as the temperature rises from 15° C. to 50° C. Between 50° C. and 60° C. the initial rate of corrosion appears to fall off very quickly, for at 60° C. it is less than at 15° C.

In every case the rate of corrosion falls off with time, and more rapidly at higher temperatures than at low. Consequently, although the initial rate of corrosion is greater at higher temperatures, the actual rate of corrosion after a given time will be smaller.

Analysis of the corrosion product at 15° C. and 50° C. indicates that at these temperatures the attack takes place in three successive stages. First there is a selective attack upon the copper; this is succeeded by a period of complete corrosion (after nine days at 15° C. and twenty days at 50° C.); the third stage is a selective attack upon the zinc. In other words, at the beginning of corrosion the rate of solution of the copper is much greater than that of the zinc. This gradually falls off; at the same time the rate of solution of zinc gradually increases. For a short time they are approximately equal; after that the rate of solution of the zinc is greater than that of the copper.

In stagnant sea water this third stage occurs more quickly at 15° C. than at 50° C. It is probably dependent upon the amount of O and CO₂ present in solution in the sea-water. It is hastened by aeration. It appears to be associated with the formation of a film of copper oxide which protects the copper but permits solution of the zinc.

(c) *Aeration of the Sea-Water.*—At temperatures up to 50° C. aeration of the sea-water increases the initial rate of corrosion. At 50° C. its effect is very slight, while at 60° C. it diminishes the rate of corrosion. The effect of aeration appears to be greatest at low temperatures. This is no doubt associated with the well-known fact that rapid localised corrosion occurs just inside the inlet end of the tubes in the coldest part of the condenser. In every case it increases the proportion of zinc in the corrosion product.

The corrosion of pure copper in sea-water is checked by aeration owing to the formation of an oxide film. On the other hand, the corrosion of pure zinc in sea-water is considerably accelerated by aeration.

(d) *Dilution of the Sea-water.*—Diluted sea-water attacks 70/30 brass more slowly than ordinary sea-water. At the same time the proportion of zinc in the corrosion product increases rapidly as the sea-water is made more dilute.

Thus after thirty-four days at 50° C. in aerated solutions of sea-water at the following concentrations, $s/1$, $s/2$, $s/4$, $s/8$, $s/16$ (where $s/1$ is the concentration of ordinary sea-water, $s/2$ being half that concentration, and so on), the percentage of zinc in the corrosion products was respectively 18.0, 24.2, 33.9, 44.1, and 58.5. In $s/1$ and $s/2$ sea-water, therefore, the copper in the brass dissolves more rapidly than the zinc, but in $s/4$, $s/8$, and $s/16$ sea-water the zinc dissolves more rapidly than the copper.

This is in agreement with the general belief that estuary waters are more selectively corrosive than the water of the open sea.

The solubility of pure copper in sea-water is diminished by dilution of the sea-water and is least in distilled water. The solubility of pure zinc in sea-water is increased by dilution of the sea-water, and is greatest in distilled water. It appears from this that the dissolved salts are responsible for the solution of copper and the water and the dissolved gases for the solution of the zinc.

Dilution of the sea-water, therefore, while retarding the actual rate of corrosion of 70/30 brass, actually promotes dezincification.

(e) *The Catalytic Action of Zinc and Copper Oxysalts.*—Moist zinc chloride at ordinary temperatures does not produce dezincification. When heated to 70° C., however, rapid dezincification is set up, owing to the formation of zinc oxychloride. When zinc chloride is added to sea-water at 40° C., in which a piece of 70/30 brass is suspended, it produces a finely divided white salt, zinc oxychloride, which gives rise to rapid dezincification of the brass similarly at 50° C.

Aerated sea-water at 60° C. produces white spots on the surface of the 70/30 brass. These white spots are found to

* A Contribution to a General Discussion on "The Corrosion of Metals," held before the Faraday Society, December 8, 1915.

cover areas of copper, showing that they have produced dezincification.

Sea-water when allowed to dry on a piece of 70/30 brass at ordinary temperatures forms a greenish blue crystalline salt which covers a pit. It does not appear to give rise to dezincification, but promotes rather the solution of copper.

Sea-water when allowed to dry on 70/30 brass at 100° C. forms a white salt which does promote dezincification.

At ordinary temperatures, therefore, the attack is greater upon the copper, and the copper oxychloride is formed. This salt catalytically facilitates the solution of copper. At high temperatures (between 80° C. and 100° C. at any rate) the attack is almost completely upon the zinc, and zinc oxychloride is formed. This salt catalytically facilitates the solution of zinc.

In connection with this fact it is interesting to note the following experiment:—A tube of 70/30 brass was heated internally by steam. Cold sea-water flowed continuously round the outer surface. At various points of the surface air-bubbles were formed. Where these air-bubbles appeared upon the surface of the hot tube rings of zinc oxychloride were formed, presumably by the evaporation of the thin film of sea-water in the presence of the air of the bubble. In some cases a succession of air-bubbles had followed one another at the same point of the surface, each producing a ring of white salt, and so gradually increasing the deposit of white salt. This might be a frequent cause of localised dezincification in condenser tubes.

(f) *The Physical Condition of the Metal.*—When 70/30 brass is hard drawn it corrodes less rapidly than when it is annealed. At the same time, however, there is a greater proportion of zinc in the corrosion product. Dezincification, therefore, occurs more readily in a hard-drawn 70/30 tube than in an annealed 70/30 tube.

(g) *Contact with Electro-negative Substances.*—Carbon or coke resting upon a clean brass surface is generally in good electrical contact with the brass. When good contact exists between the two the rate of solution of the brass is increased fivefold, and the proportion of zinc in the corrosion product rises to 60 per cent. At the same time the surface of the metal becomes covered with a loosely adherent red film of copper oxide, which can be removed by a mere touch of the finger. The effect produced by contact with coke is much greater at 50° C. than at 15° C. The e.m.f. between coke and 70/30 is about 0.19 volt. Between coke and zinc there is an e.m.f. of about 1 volt.

Other substances, electrically neutral, such as string or brick, act as loci for the accumulation of oxysalts of Zn and copper, and so lead to accelerated local corrosion.

A piece of coke fixed in a condenser tube might accelerate selective corrosion in three ways:—

(a) If contact were good it would exert an electrochemical action.

(b) By obstructing the free passage of the water in the tube it would lead to a greatly increased temperature along that part of the tube between the coke and the inlet end. This would facilitate general dezincification of that portion of the tube.

(c) The water on the outlet side of the coke would only be able to trickle along the tube, and the continuous film evaporation to which it would be subjected would, if the tube were hot enough, produce deposits of zinc oxychloride. This also would facilitate dezincification of the tube.

Other cases in which corrosion, particularly selective corrosion, is localised at certain points along a condenser tube appear to be due to a lack of homogeneity in the metal itself. Perhaps local e.m.f.'s are set up between areas containing dissolved copper oxide and the remaining portion of the tube. The presence of strained metal in the hard-drawn alloy may be a contributory factor in the early stages of corrosion. It is generally noticed that the white spots of zinc salt, which indicate the occurrence of

dezincification, always occur first along the drawlines and upon the filed edges of the test-pieces.

A general consideration of the foregoing facts conveys the impression that a solid solution of zinc and copper is intermediate in character between a physical mixture and a chemical compound. The copper and the zinc retain to a very large extent their own characteristic individuality, but in each case it is modified by the presence of the other constituent. It is as though there were some kind of weak chemical combination (or rather physical combination, since the chemical character of the constituents is not changed entirely but only modified) between the two, whereby the available energy of each is diminished.

In 70/30 brass the diminution of the available energy of the zinc is of course greater than in the case of the copper, for the influence which is exerted by a dissolved metal upon the character of the solvent metal is a function of the atomic volume. In the case of zinc and copper the atomic volumes are practically equal and the influence of each constituent upon the other becomes a function of the concentration. When, however, the proportions of zinc and copper are equimolecular the available energy of both is reduced to a minimum, and the rate of corrosion at ordinary temperatures becomes practically zero.

In the alloys containing more than 50 atoms per cent of copper it is the copper which dissolves at first, although zinc is more rapidly soluble in sea-water. This suggests that the chemical activity of the zinc is neutralised in the solid solution.

The electrode potential of zinc in sea-water at 16° C. is -0.5100 volt and of copper +0.3896 volt. That of 70/30 brass is +0.3460 volt, and therefore resembles copper rather than zinc. Similarly, the chemical activity of the copper is reduced considerably by the presence of the zinc in solid solution, and appears to reach a minimum when the atomic concentration of the zinc exceeds 50 per cent.

The strength of any combination between copper and zinc and the influence exerted by it upon the properties of the constituents would depend upon—

(a) The composition of the alloy. By which is meant the concentration of zinc and copper in the alloy and the presence of other metals, such as iron and tin, and of non-metals, such as oxygen.

(b) The physical state of the alloy, *i.e.*, whether it is solid or liquid, amorphous or crystalline.

(c) The physical environment of the alloy, its temperature and pressure.

(d) The chemical environment of the alloy, which in this case refers to the nature and composition of the corroding solution.

Is it possible that a compound or compounds of copper and zinc exist stable only at low temperatures—say below 50° C.? These may dissociate into a system of solid solutions as the temperature rises and the composition is altered.

Such a conception appears to afford a reasonable explanation of the corrosion of 70/30 brass. Its application to other fields of investigation does not come within the scope of this paper.

Institute of Chemistry.—*Pass List; January (1916) Examinations.*—The results of the Examinations of the Institute of Chemistry recently held in London have now been published. Three candidates passed the Intermediate Examination, *viz.*, H. E. Cox, B.Sc. (Lond.); A. J. Somer; and E. E. Wells, B.Sc. (Lond.). Nine candidates passed the Final (A.I.C.) Examination, *viz.*:—In the Branch of Mineral Chemistry—R. G. Browning, B.Sc. (Lond.) In the Branch of Organic Chemistry—R. Brightman; R. L. Brown, A.R.C.S.I.; H. S. Foster; and A. Hancock. In the Branch of the Chemistry (and Microscopy) of Food and Drugs, Fertilisers, and Feeding Stuffs, Soils and Water—C. E. Corfield; J. J. Geake; F. A. Pickworth, B.Sc. (Lond.); and Fred Smith.

THE PERMANGANATE AND IODIMETRIC DETERMINATION OF IODIDE IN PRESENCE OF CHLORIDE AND BROMIDE.*

By O. L. BARNEBEY.

THE permanganate oxidation of iodide to iodate originated with Pean de Saint Gilles (Ref. 1). A large number of modifications of this method have been made, but they still retain the fundamental idea of conversion of iodide to iodate. Certain authors use other oxidising agents, such as nickelic oxide (2), potassium dichromate (3), chlorine (4) to accomplish the same purpose.

Theoretically this reaction has many points in its favour, the essential one being its application to the estimation of small quantities of iodides. For this purpose the addition of three oxygen atoms to the iodide demands a sufficiently large quantity of oxidising agent to make the titration quite accurate. The measure of the amount of oxidising agent required or of the iodate formed gives two means for the quantitative determination of iodides.

Pean de St. Gilles (5) determined the quantity of iodide by adding an excess of permanganate to the neutral or alkaline solution, heating a few minutes, adding an excess of ferrous sulphate containing sulphuric acid, and then titrating the excess of ferrous iron remaining in the solution. Hence the original method consists of a measure of the oxidation of iodide to iodate from the quantity of permanganate required. Klemp (6) adds zinc chloride to facilitate precipitation of the manganese and watches for the appearance of the permanganate colour in the supernatant liquid. The end-point is obscure, however, and continuous heating and cautious addition of permanganate is required to obtain even a moderately good result. Reinige (7) determined the excess of permanganate with sodium thiosulphate. Sonstadt (8) precipitates the iodic acid formed by this reaction with barium chloride, transforms the barium iodate with potassium sulphate to potassium iodate, and then estimates the amount of iodate either "gravimetrically or iodimetrically." Other investigators have destroyed the excess of permanganate with such agents as alcohol (9) or hydrogen peroxides (10), filtered out the hydrated manganese dioxide, and then titrated the iodic acid in the filtrate iodimetrically. Sodium sulphite (11) has been used to reduce the permanganate, later reducing iodic to hydriodic acid and converting to silver iodide. McCulloch (12) pointed out that the measure of the available oxygen from the hydrated manganese precipitate gives erroneous results, inasmuch as the precipitate is not pure manganese dioxide, but contains some manganous manganese. This condition of mixed oxides is one that might be anticipated from the general chemistry of the oxides of manganese. The oxide precipitated by the interaction of a reducing agent on permanganate or manganate or by an oxidising agent on manganous manganese almost, if not invariably, contains part of its manganese in a lower state of oxidation than four (13). The titration of iodic acid iodimetrically with thiosulphate, after removal of the excess of permanganate by alcohol or similar reducing agent, and subsequent removal of the resulting manganese dioxide by filtration, removes the difficulty of an inconstant manganese oxide product of reaction and lessens filtration troubles, inasmuch as a considerable excess of permanganate can be employed, and heating continued if necessary until the solution is quite easily filtered. The use of hydrogen peroxide (14) or alkali sulphites (15) for the removal of the excess of permanganate would necessitate great care to avoid reduction of an appreciable amount of iodate, as these reducing agents are used to effect quantitative reduction of iodate to iodide.

Investigators using chlorine or hypochlorite have removed the excess of oxidising agent by means of a current of air (16), boiling (17), or phenol (18). However, the

general idea remains the same, conversion of the iodide to iodate and ascertaining the quantity of iodate formed.

The investigation to be outlined in the following pages is divided into two parts:—(1) the permanganate titration according to the original and modified method of Pean de Saint Gilles, and (2) the iodimetric titration of the iodate formed by the permanganate oxidation of the iodide.

1. The Permanganate Titration of Iodides.

The success or failure of the permanganate method as outlined by Pean de Gilles is dependent for the most part on the quantitative oxidation of ferrous to ferric iron by the permanganate in the presence of chloride and bromide. When the titration of ferrous iron with permanganate is attempted in the presence of halides in acid solution free halogen is liberated, the ease with which this liberation occurs increasing in the order hydrochloric, hydrobromic, and hydriodic acids. The effect of chlorides has been studied by a number of investigators (19), and various reagents have been used to prevent the detrimental influence of chlorides. Manganous salts have been found to be particularly effective. The author finds that manganous salts (20) also prevent the evolution of bromine, the best results being obtained in phosphoric acid solution.

If an alkaline solution containing chloride or bromide and permanganate is treated with ferrous sulphate acidified with sulphuric acid, chlorine (or hypochlorous acid) or bromine is liberated. If the acid ferrous sulphate solution is added in sufficient quantity all at once, thus ensuring acidity only when the iron solution can give reduction at the same instant as acidity, then the liberation of halogen is greatly diminished. However, if sufficient manganous sulphate is added to the ferrous sulphate solution, which contains phosphoric acid, before the ferrous iron solution is added to the permanganate solution, then the tendency toward halogen liberation can be completely eliminated. The ferrous iron in the resulting solution can then be titrated accurately with permanganate.

Several series of analyses, in which the time of heating the iodide with permanganate was studied, showed that the heating should be continued a few minutes after the solution reached boiling temperature. Five minutes sufficed in every case. The effect of varying alkalinity was also tried and a low concentration of alkali found to give the best results. In acid solutions free iodine is liberated, which is transposed to iodic acid in part. If the concentration of acid is low some iodine is liberated, complete conversion to free iodine being effected when the acid attains sufficient strength. In neutral solution the transposition is complete to iodic acid, but more time is required than in alkaline solution. Inasmuch as strong alkaline solutions of permanganate on heating decompose to a greater or less extent, liberating oxygen, a 0.01/N solution of sodium hydroxide was chosen for this work, 1 cc. of normal alkali being added for each 100 cc. of solution present. Heating just below boiling for five minutes a 0.01/N sodium hydroxide solution containing a moderate amount of permanganate (10 to 20 cc. of 0.1/N solution) causes a loss of oxygen which is so small as to be negligible. In fact such solutions give very little loss when heated for sixty minutes.

When a considerable quantity of iodic acid is treated with a large excess of ferric iron in acid solution more or less reduction of the iodate occurs, simultaneously oxidising the iron and liberating free iodine. To ascertain the extent of the reducing effect of ferrous iron on iodic acid in the presence of varying concentrations of sulphuric and phosphoric acids, a series of experiments was performed (Table I.). In this series the quantity of potassium iodate was kept constant throughout, and the other factors varied in a systematic manner. Each experiment was performed at room temperature. Each solution was allowed to stand five minutes after mixing the reagents. The volume before titration was 200 cc. in each case.

* *Journal of the American Chemical Society*, xxxvii., No. 6.

TABLE I.—*Reduction of Iodic Acid by Ferrous Sulphate.*
1 cc. $\text{KMnO}_4 = 0.009208$ grm. Fe.
1 cc. $\text{FeSO}_4 = 0.658$ cc. KMnO_4 .
50 cc. of 0.1/N KIO_3 (3.5678 grms. per litre) used in each experiment.

Normality.		Iron (grm.)		
H_2SO_4 .	H_3PO_4 (a)	Present.	Found.	Error.
0.5	—	0.0606	0.0608	+0.0002
0.5	—	0.1212	0.1213	+0.0001
0.5	—	0.1818	0.1818	0.0000
0.5	—	0.2424	0.2422	-0.0002
0.5	—	0.3030	0.3029	-0.0001
—	0.5	0.0606	0.0606	0.0000
—	0.5	0.1212	0.1213	+0.0001
—	0.5	0.1818	0.1818	0.0000
—	0.5	0.2424	0.2420	-0.0004
—	0.5	0.3030	0.3029	-0.0001
1.0	—	0.0606	0.0608	+0.0002
1.0	—	0.1212	0.1212	0.0000
1.0	—	0.1818	0.1814	-0.0004
1.0	—	0.2424	0.2414	-0.0010
1.0	—	0.3030	0.3011	-0.0019
—	1.0	0.0606	0.0610	+0.0004
—	1.0	0.1212	0.1212	0.0000
—	1.0	0.1818	0.1812	-0.0006
—	1.0	0.2424	0.2410	-0.0014
—	1.0	0.3030	0.3011	-0.0019
1.5	—	0.0606	0.0608	+0.0002
1.5	—	0.1212	0.1208	-0.0004
1.5	—	0.1818	0.1812	-0.0006
—	1.5	0.0606	0.0608	+0.0002
—	1.5	0.1212	0.1197	-0.0015
—	1.5	0.0606	0.0608	+0.0002
—	2.5	0.1212	0.1200	-0.0012

(a) Computed on the basis of three replaceable H atoms.

All the low results of this series were caused by a partial oxidation of ferrous iron by the iodic acid, more or less odine being visible at the end of the five-minute period preceding titration. In no case was iodine liberated at once. These results indicate that the solution should not have an acidity with sulphuric or phosphoric acid greater than normal, and that not more than 0.1 grm. of ferrous iron should be added in excess if five minutes are to be allowed to intervene between the time of adding the excess of iron salt and titration of that excess with permanganate. However, much larger quantities of both ferrous iron and sulphuric or phosphoric acids can be present if the excess of ferrous iron is titrated immediately.

Table II. gives the results of actual analyses of known amounts of potassium iodide, thus showing the combined effect of manganese dioxide and potassium iodate on the decomposition of potassium permanganate, and also obtaining a further check on the reduction of iodic acid by ferrous iron. The potassium iodide was measured into an Erlenmeyer flask and 1 cc. of N NaOH added, followed by the permanganate. The solution was heated to boiling, and kept just below ebullition for the time designated. After cooling in running water the mixed solution of 50 cc. of ferrous sulphate (1 cc. = 0.802 cc. KMnO_4) plus 25 cc. of manganese preventive solution (60 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 250 cc. H_3PO_4 of sp. gr. 1.70 per litre) was added. The time interval of standing previous to titration was about ten minutes in each experiment. No iodine was visible before titration, which showed that no reduction of iodic acid had taken place.

The results given in Tables I. and II. allow at least three conclusions:—(1) The loss due to heating of the alkaline solution is negligible; (2) the reducing action of ferrous iron on the iodic acid can be made inappreciable; and (3) accurate determinations of iodide can be made by

using the mixed solution containing some manganese salt and ferrous sulphate to remove the excess of permanganate as well as the hydrated manganese dioxide, the excess of ferrous iron being subsequently titrated with permanganate.

TABLE II.—*Permanganate Determination of Iodide in Pure Potassium Iodide.*

1 cc. $\text{KMnO}_4 + 0.005648$ grm. Fe = 0.002798 grm. KI.
1 cc. $\text{KMnO}_4 = 0.8020$ cc. FeSO_4 .
0.01 N KI = 1.66 grm. KI per litre.

0.01 N KI Cc.	0.01 N Cc.	Time. Mins.	KMnO ₄ required for—			KI (grm.).	
			Excess. Cc.	FeSO_4 . Cc.	KI. Cc.	Present.	Found.
1.	50	60	5	9.60	40.10	0.0830	0.0825
2.	50	60	15	9.64	40.10	0.0830	0.0827
3.	50	60	30	9.64	40.10	0.0830	0.0827
4.	50	60	60	9.64	40.10	0.0830	0.0827

TABLE III.—*Permanganate Determination of Iodide in Mixtures with Chloride and Bromide.*

1 cc. $\text{KMnO}_4 = 0.005648$ grm. Fe.
1 cc. $\text{KMnO}_4 = 0.8275$ cc. FeSO_4 .
1 cc. KI = 0.00166 grm. KI.

	0.1 N	0.1 N	MnSO ₄ .	H ₃ PO ₄ .	KI (grm.).		
	KBr. Cc.	NaCl. Cc.			Present.	Found.	Error.
1.	10	—	10	15	0.0830	0.0828	- 0.0002
2.	30	—	10	15	0.0830	0.0827	- 0.0003
3.	60	—	10	15	0.0830	0.0828	- 0.0002
4.	100	—	10	15	0.0830	0.0831	+ 0.0001
5.	5 (a)	—	10	15	0.0830	0.0828	- 0.0002
6.	10 (a)	—	50	15	0.0830	0.0838	+ 0.0008
7.	20 (a)	—	100	25	0.0830	0.0827	- 0.0003
8.	—	50	10	15	0.0830	0.0027	- 0.0003
9.	—	10 (b)	50	25	0.0830	0.0827	- 0.0003
10.	50	50	10	15	0.0017	0.0018	+ 0.0001
11.	50	50	10	15	0.0033	0.0035	+ 0.0002
12.	50	50	10	15	0.0083	0.0086	+ 0.0003
13.	50	50	10	15	0.0166	0.0168	+ 0.0002
14.	50	50	10	15	0.0415	0.0414	- 0.0001
15.	50	50	10	15	0.0830	0.0827	- 0.0003

(a) KBr, grms.

(b) NaCl, grms.

In Series III. 50 cc. portions of 0.01/N potassium iodide solution were treated in an Erlenmeyer flask with permanganate in excess in the presence of bromides and chlorides, added in the form of 0.1/N potassium bromide and 0.2/N sodium chloride, or of the solids. One cc. of N sodium hydroxide was added, the solution heated, and potassium permanganate added until there was about 10 cc. excess; then the solution was heated for about five minutes. The solution was cooled and the ferrous sulphate solution (containing 250 grms. per litre of manganous sulphate) was added in sufficient quantity to be about 10 cc. in excess. After complete solution of the manganese dioxide phosphoric acid (1:3) was added. The excess of ferrous iron was then titrated with the permanganate.

In Sample 6 the end-point was blurred because of liberation of free bromine, the odour of which was distinct. MnSO_4 was not present in sufficient amount to take care of the large amount of KBr added originally. In other titrations concordant results were obtained.

In Series IV. 0.001/N potassium iodide was used with 0.001/N permanganate and 0.001/N ferrous sulphate. The method of procedure was the same as with 0.01/N potassium iodide. One cc. of N sodium hydroxide and 5 cc. of preventive solution (200 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 350 cc. H_3PO_4 of sp. gr. 1.7 per litre) were employed in each case. The total volume was 100 cc. for each titration. Considerable care was found to be necessary to exclude foreign impurities when dealing with such weak solutions of permanganate. Only recently boiled water, previously distilled from alkaline permanganate, was employed. The titrations were continued carefully to the first definite

pink colour, and the amount of permanganate necessary to give the same pink colour in a blank experiment was subtracted.

TABLE IV.—*Permanganate Determination of small amounts of Iodide in Halide Mixtures.*

	0.1 N KBr. Cc.	0.1 N NaCl. Cc.	KI (grm.).		
			Present.	Found.	Error.
1.	5	5	0.00017	0.00016	-0.00001
2.	5	5	0.00033	0.00033	0.00000
3.	5	5	0.00083	0.00080	-0.00003
4.	5	5	0.00166	0.00167	+0.00001
5.	5	5	0.00083	0.00082	-0.00001

Correct results are thus seen to be possible with very small quantities of iodides.

(To be continued).

FIXATION OF ATMOSPHERIC NITROGEN.*

By LELAND L. SUMMERS.

(Continued from p. 27).

III. Description of Processes.

THREE processes which have been commercially applied for directly preparing nitric acid from atmospheric nitrogen are: First, Birkeland-Eyde; second, the Schonherr, and third, the Pauling. These are diagrammatically shown in Figs. 2, 3, and 4. Fundamentally all operate on the same principle of forcing air into intimate contact with a high-tension arc and withdrawing the product nitric oxide, NO, as directly and rapidly as possible in order to reduce the amount of decomposition of the resulting product. As these processes have been repeatedly described in detail in the technical press, we will confine our attention to general comparisons.

Birkeland-Eyde Process.—The Birkeland-Eyde furnace, illustrated in Fig. 2, has been the most extensively used. Its most distinctive features are the use of the magnets A, which distort the arc into a series of great wheels of flame, extending radially outward from the electrodes E, located normal to the paper in Fig. 2. The air enters through the conduit c and is distributed to the arc through the holes in the firebrick lining. The products are withdrawn from around the periphery at D. The voltage of 10,000 volts is reduced by an inductive reactance coil to about 5500 volts across the electrodes. The alternating current of 50 cycles establishes the arc across the U-shaped water-cooled electrodes E, spaced about 0.3 in. (8 mm.) apart, and a flow of current takes place across this ionised path, the electrons formed being repelled by the intense magnet field of the direct-current magnets, A, and their discharge radially outward causes the arc stream to follow until it is deflected outward in a great semicircle. As its length is thus increased, the potential across the electrodes rises and a second arc is established, the effect being to make a series of rapidly expanding arcs which are expanded across the entering air spaces. As the arcs travel radially outward, the contact of the ionised arc stream with the incoming air disrupts the nitrogen molecule and causes the formation of NO, and the gaseous products travel rapidly to the periphery of the furnace, where they are withdrawn at an average temperature of about 1250° C. The earlier Eyde furnaces were of 300 kw. capacity and gave a concentration of about 1.5 per cent. NO and a yield of about 500 kg. of nitric acid per kw. per year. The more recent furnaces are of 3000 kw. capacity and give concentration of about 2 per cent NO and a yield of 580 to 600 kg. of nitric acid per kw. per year, or 65 to 70 grms. of nitric acid per kw.-hr.

Schonherr Process.—The Schonherr furnace (Fig. 3) consists of a long iron pipe, having an electrode E inserted in the bottom, and the tube itself is the other electrode, the distinctive feature of the process being that an alternating current at 4500 to 5000 volts maintains an arc of from 23 to 25 feet (7 m. to 8 m.). The furnace is started by forming an arc from the lower electrode to the wall of the iron pipe by means of a lever Z, a blast of air is then admitted to the pipe, whereupon the ionised gases are caused to ascend and carry with them the arc stream. In this way the arc is caused to travel toward the upper end of the tube, where it is maintained. In practice, the air stream is admitted in a tangential direction, causing a whirling motion to be imparted to the air surrounding the arc; this creates a vortex motion, causing the arc to be surrounded by the cooler air and thus protects the iron pipe which is wholly unlined. The rapid passage of the

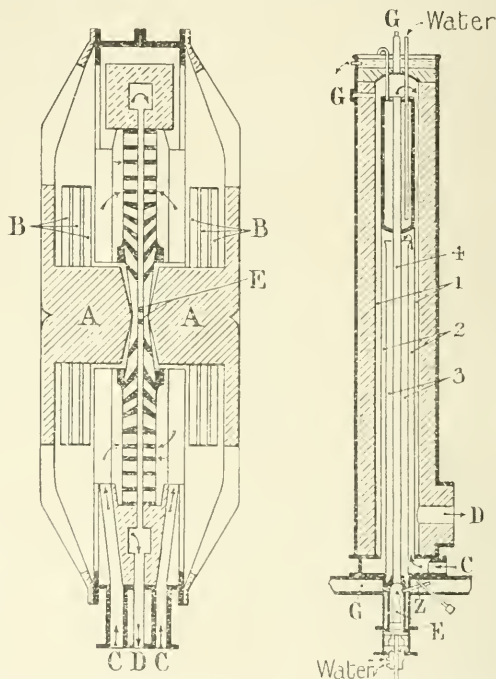


FIG. 2.—BIRKELAND-EYDE.
A, core; B, windings; C, gas entrance;
D, exit.

FIG. 3.—SCHONHERR
FURNACE.

air maintains an ionised path for the arc stream, and the arc burns quietly. The products are withdrawn from the upper end and pass downward through the passes 1 to the outlet D. Previous to being withdrawn they are cooled by the water cooler and are further used to preheat the entering air. The temperature of the exit gases is about 850° C. Provision is made for preheating the air by passing it upward in the space 2 of the casing and then downward to a point opposite the electrode. The largest furnaces are of 800 kw. capacity and maintain an arc about 23 feet (7 m.) long. They give an NO concentration of about 2.25 per cent and a yield of 550 to 575 kg. per kw.-year or 65 grms. per kw.-hr.

Pauling Process.—The Pauling furnace (Fig. 4) establishes an a.c. arc of 4000 volts between two curved horns, much after the pattern of the horn type lightning arrester. This arc when established is driven upward by a blast of air admitted at B and is disrupted by the diverging horns. A sheet of arc flame is maintained by re-establishing a new arc, as the previous one is elongated. The effect is to create an arc flame about 30 in. (75 cm.) high and to

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have this flame in intimate contact with the rapid moving air used to blast the arc flame. Two furnaces are usually operated together, and to assist in a rapid cooling of the products, a portion of the previously heated or partially cooled discharged gases are admitted to the top of the furnace. The arc is established by the high voltage breaking down the gap between narrow blades *c*, located in the horn gaps, and as these wear away, they are continually advanced by the adjustments *d*. The percentage of NO obtained is 1.25 to 1.5 per cent in the 400 kw. furnace, while the yields are 525 to 540 kg. per kw.-year or 60 grms. per kw.-hr.

Power Factor and Electrode Wear.—In all these processes where the arc is distorted the power factor is about 70 per cent, being about 5 per cent lower in the Schonherr type, apparently due to inductive effects of the iron pipe surrounding the arc. In both the Pauling and Schonherr furnaces the electrodes are adjustable and the air blast plays directly on the electrodes, necessitating this adjustment and also means of easy renewals. The Pauling blades last less than twenty-four hours. The Schonherr electrode is a straight rod of iron and is fed upward as it burns away. The Eyde water-cooled copper pipe not being directly in the path of the air blast lasts three to four weeks. In the operation of both the Eyde and Schonherr furnaces a furnace is placed on each separate leg of the three-phase circuit, so that six wires are used for each generator. In the installations that have been made the furnaces are connected direct without transformers, and as no parallel operation of generators is attempted, a large number of cables are required between the power-house and the furnaces.

Efficiency and Losses.—It will be noted that notwithstanding the radically different types of these furnaces there is not a wide divergency in the yields, the Schonherr furnace showing the highest concentration of NO, while the Eyde probably produces a slightly higher output per kw.-hr. All of these concentrations indicate that the maximum temperature of the arc is not utilised, but is very considerably reduced by the large amount of air admitted. If the temperature of the arc is raised by admitting less air, there is a heavier decomposition of the products, and all products are heated to a higher temperature with a corresponding loss, the net result being a lower yield per kw.-hr. As the yield per kw.-hr. is of fundamental importance, adjustments are governed accordingly. The concentration of NO affects directly the apparatus for recovering the products, such as the absorbing towers, and the lower the concentration of NO the greater the losses from heating the inert gases. The furnace efficiency will largely be determined by this factor. Let us take for example a concentration of 1.75 to 2 per cent NO and examine the distribution of heat. If we take the specific heats of a molecule of the diatomic gases as constant, there will be no difference in the specific heats per molecule of N, O, or NO, and taking a standard value for this, we may calculate the heat energy expended. Let us assume, following Haber, that for a change of temperature *t*, the specific heat per molecule will be—

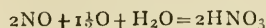
$$6.8 + 0.0006 t.$$

The gaseous products heated in the furnace with 1.75 to 2 per cent NO concentrations will have, from Nernst constants, an absolute temperature of about 2500°, and the air would have an initial temperature say of 27° C., or 300° absolute, so the arc would raise the temperature of the 100 molecules through 2200°, or,

$$\text{sensible heat} = 100 (6.8 + 0.0006 t \times 2200) 2200 \\ = 1,786,400 \text{ calories.}$$

As two molecules of NO require a latent heat of formation of 43,000 calories, the total heat will be 1,829,400 gm.-calories; and as one watt hour equals 860 gm.-calories, the energy represented will be equal to 2.12 kw.-hr. for two gm.-molecules of NO. Taking the atomic weight of N as 14 and of O as 16, the gm.-molecule of NO will weigh 30 grms., so 2.12 kw.-hr. will form 60 grms. of NO.

If we mix this NO with air and water it will form nitric acid without requiring a further expenditure of energy, thus,



and the 60 grms. of NO will then become 126 grms. of HNO₃; the production of nitric acid will then be 126 grms. per 2.12 kw.-hr. or 59.4 grms. of HNO₃ per kw.-hr. Of this expenditure of 2.12 kw.-hr. the formation of the nitric oxide utilised

$$\frac{43,000}{1,829,400} = 2.35 \text{ per cent,}$$

and the sensible heat imparted to the active gases to raise their temperature to form two molecules of NO required 35,728 calories, so this represented

$$\frac{35,728}{1,829,400} = 1.95 \text{ per cent,}$$

while the heating of inert nitrogen and oxygen, or that portion of the air which was not utilised, but which was heated to the furnace temperature, was represented by

$$\frac{1,750,672}{1,829,400} = 95.7 \text{ per cent.}$$

These calculations, while open to some criticism on account of the uncertainty of the figures for specific heat and its change with temperature, closely approximate the conditions, and indicate that low concentrations of NO, when formed from thermal reactions, are extremely wasteful. If concentrations of 10 per cent NO are obtained with temperatures of 4200° to 4300° C., the yields may be increased to 135 to 140 grms. of HNO₃ per kw.-hr., but the greatest saving in energy will result in utilising other than purely thermal energy. While thermal energy may be produced more cheaply directly from fuel, its temperature possibilities are again limited by the inert gases of combustion if air is the source of these.

Hausser has commercially applied a process for utilising coke oven gases by means of an explosion bomb. The amounts of excess gases may be limited, and the intimate mixture of combustible and oxygen due to pre-compression of the charge permits of high combustion temperatures being reached. Fig. 5 shows this bomb having a capacity of 1600 cc. The gases, either illuminating or coke oven gases, enter through the inlet after previously exhausting the air by means of the air pump outlet. Means are provided at A for injecting under high pressure a spray of water to cool the products as quickly as possible. The ignition takes place at 2 by means of a high-tension spark, and the explosion is propagated outward from this point and the vapour condenses on the enamel lining of the bomb.

With this device Hausser obtained a temperature of 2100° K, and concentrations of NO of 0.5 per cent. The temperature calculated from the assumed figures for specific heat indicated a concentration of 0.3 per cent for equilibrium by the Nernst calculation, and Hausser sought to explain this increase of yield as due to a chemical reaction induced by photo-chemical effects similar to the ionisation by the ultra-violet or actinic rays of light. The maximum yields were 99 grms. of HNO₃ per cub. m. of gas, or equivalent to 6.2 lb. of HNO₃ per 1000 feet of gas. A commercial plant on this system has been installed in Germany. This low concentration of NO greatly complicates the commercial application, as the absorbing devices are more cumbersome and the percentages of loss are higher.

(To be continued).

University College.—The Provost informs us that, owing to circumstances arising out of the war, Mr. Kilburn Scott's course on "Electrical Production of Nitrates for Fertilisers and Explosives," announced to begin on Wednesday, January 26, will not be held.

WINE ANALYSIS.*

ANY fermented fruit juice will produce a wine. Cleanliness, temperature, and the yeast having the upper hand in the fermentation all have their influence on the final product.

Lack of cleanliness fosters vegetable fungus growths that create undesirable fermentations and spoil the wine.

Temperature influences the final product in that at 25° to 30° C. a rapid fermentation is produced, while at 10° to 15° C. a slower one is produced. The rate of fermentation affects the bouquet which is due to the ethers. The higher temperature will give less bouquet or aroma than the lower.

The races of yeast, having the upper hand in the fermentation differ from one another in the products of their fermentation. A wine must, fermented by Jørgensen with different yeasts, varied from 2 to 14 per cent of the total alcohol produced in the glycerin content. The fact that races of yeast differ so in the yield of their fermented products has led European governments as well as the United States to make extensive experiments with races of yeast to discover those that will give the most desirable qualities. These yeasts are kept and furnished to applicants by bureaus established for that purpose.

Wines are either natural or fortified. The natural wines are those to which no sugar or alcohol has been added, but have been allowed to ferment to the exhaustion of the sugar or yeast nutriment, or have been checked by the strength of the alcohol developed. 14 per cent strength of alcohol by weight is about the limit to which a yeast can ferment in a wine must. Hock, claret, and many California wines are natural. Fortified wines are those to which sugar has been added, as is often done when a poor year has lowered the sugar content of the grapes. The amount added is generally controlled by law in this country as well as in Europe. Alcohol, too, is very often added. The spirit is generally added before fermentation is completed. The strength is then raised and fermentation is checked. The wine thereby is often made sweet, due to the unfermented sugars. Madeira, sherry, and port are examples of fortified wines.

Wines are also classified by colour, taste, and by their positive or negative effervescence. We have the red or white wines, dry or sweet, and still or sparkling.

Burgundy, clarets, and Bordeaux wines are red, while the Rhenish, Moselle, and Sauternes are white. The skins of the grapes give the colouring matter and are fermented with the pulp before pressing. White wine is made from the pressed pulp freed from the skins at once, or is made from white grapes.

Dry wines are those in which all the sugar has become exhausted by fermentation while sweet wines contain various amounts of unfermented sugar. Madeira, red or white, is a dry wine, while port is an example of a sweet wine. Still wines are those from which carbon dioxide has been exhausted so there is no effervescence. Sparkling wines effervesce due to carbon dioxide and are either heavily charged artificially, or the gas is formed by the addition of sugar to the bottles before corking.

In the making of grape wine the quality depends on the care exercised in grading the grapes and careful regulation fermentation. The grapes are crushed by machinery, and in some localities by the bare feet. The juice is then pressed from the pulp by machinery.

König's analysis of a large number of grape musts is here summarised below :—

	Minimum.	Maximum.	Mean.
Specific gravity..	1.0690	1.2075	1.1024
Water (per cent) ..	51.53	82.10	74.49
Nitrogenous material ..	0.11	0.57	0.28
Sugar ..	12.89	35.45	19.71
Acid ..	0.20	1.18	0.64
Other non-nitrogenous material	1.68	11.62	4.48
Ash ..	0.20	0.63	0.40

* Methods of Analysis used in the Laboratories of the Armour Institute of Technology. From the *Chemical Engineer*, xxi., No. 2.

TABLE I.

	Number of analyses.	Specific gravity.	Alcohol by weight.	Extract.	Total acid as tartaric.	Free tartaric acid.	Cream of tartar.	Volatile acid as acetic.	Sugar.	Glycerin.	Nitrogen.	Ash.	P ₂ O ₅ .	Potash.	Lime.	Magnesia.	Sulphuric acid.
Germany—																	
Moselle ..	14	0.9964	7.99	2.24	0.79	—	—	—	0.031	0.72	—	0.175	0.036	0.068	0.011	0.02	0.012
Rhine ..	23	1.0005	8.00	2.60	0.81	—	0.20	—	—	0.85	—	0.23	0.046	0.085	0.017	0.022	0.020
Baden ..	46	—	6.65	2.16	0.91	0.018	0.358	—	0.095	0.49	—	0.207	0.025	—	—	—	—
Württemberg white wine	15	0.9995	6.10	2.27	0.95	0.095	0.262	—	—	0.57	—	0.20	0.043	—	—	—	0.009
Württemberg red wine ..	6	—	4.73	2.64	1.14	0.091	0.026	—	—	0.40	—	0.25	0.040	0.108	0.024	0.010	0.08
Alsace ..	15	—	6.59	2.07	0.606	0.018	0.168	0.052	—	0.55	0.028	0.29	0.038	—	—	—	—
Lorraine red wine ..	10	0.9967	8.08	2.27	0.56	0.032	—	0.155	0.088	0.50	0.019	0.185	0.030	—	—	—	0.008
France—																	
Red wine ..	29	0.9982	7.80	2.56	0.57	—	—	—	0.30	0.73	0.043	0.248	0.030	0.106	0.101	0.018	0.033
White wine ..	5	0.9963	8.30	3.03	0.66	—	—	—	—	0.97	—	0.25	0.032	0.098	0.010	0.015	0.038
Austria—																	
Tyrol red wine ..	60	0.9940	9.08	2.34	0.62	—	—	—	—	0.65	0.021	0.222	0.027	—	—	—	0.023
Tyrol white wine..	17	0.9927	8.84	1.87	0.59	—	—	—	—	0.65	0.020	0.175	0.022	0.077	—	—	0.023
Russia—																	
Red wine ..	10	0.9939	10.76	2.76	0.56	—	—	0.142	—	0.64	0.036	0.267	0.027	0.111	—	—	—
White wine ..	12	0.9931	11.96	2.568	0.49	—	—	0.100	0.458	0.59	0.026	0.204	0.030	0.086	—	—	—
Italy ..	20	—	10.61	3.44	0.52	—	—	—	1.44	0.45	—	0.29	0.032	0.115	0.009	0.017	0.019
Spain—																	
Ordinary red wine	7	—	12.30	3.53	0.49	—	—	—	0.38	1.09	—	0.61	0.027	0.242	0.008	—	0.221
Sweet wine ..	4	1.0233	12.78	9.69	0.59	—	—	—	6.55	0.63	—	0.74	0.039	0.296	—	—	0.212

Germany—

France—

Austria—

Russia—

Italy ..

Spain—

TABLE II.

	Sp. gr.	Per cent alcohol by volume.	Grms. per 100 cc.		Glycerin-alcohol ratio.	Total acids.	Extract.	Polarisation.	Reducing sugar.	Grms. per 100 cc.			
			Alcohol.	Glycerin.						Potassium sulphate.	Proteids.	Tannin and colouring matter.	Ash.
RED WINES.													
Bordeaux or claret type (81 samples)—													
Maximum ..	1.0020	15.09	11.97	0.852	8.7 : 100	0.888	3.81	—2.1	0.628	0.1570	0.5544	0.358	0.429
Minimum ..	0.9900	8.92	7.09	0.330	3.4 : 100	0.368	2.09	—0.5	0.040	0.0470	0.1865	0.064	0.209
Rhine type (6 samples)—													
Maximum ..	0.9970	13.82	10.96	—	—	0.718	3.34	—	—	—	—	0.349	—
Minimum ..	0.9940	11.00	8.73	—	—	0.358	2.69	—	—	—	—	0.211	—
Red Burgundy type (25 samples)—													
Maximum ..	0.9962	15.48	12.29	0.956	7 : 100	0.762	3.46	—1.7	0.418	0.2515	0.4482	0.328	0.416
Minimum ..	0.9911	8.00	6.35	0.461	4.7 : 100	0.408	2.10	—0.5	0.030	0.0455	0.1864	0.033	0.188
Southern French type (92 samples)—													
Maximum ..	1.0050	19.28	15.30	—	—	0.834	6.88	—	—	—	—	0.344	0.430
Minimum ..	0.9900	8.07	6.40	—	—	0.201	1.91	—	—	—	—	0.050	0.202
WHITE WINES.													
Rhine wine type (87 samples) —													
Maximum ..	1.0020	14.57	11.57	0.971	10.2 : 100	0.788	4.38	—3.5	0.626	0.1771	0.5164	—	0.447
Minimum ..	0.9883	5.00	3.98	0.474	4.6 : 100	0.327	1.51	—0.2	0.060	0.0633	0.0989	—	0.140
Sauterne type (55 samples)—													
Maximum ..	1.0157	15.20	12.07	0.904	7.7 : 100	0.766	6.78	+0.6	3.569	0.1648	0.3809	0.087	0.368
Minimum ..	0.9892	8.23	6.53	0.178	1.8 : 100	0.377	1.69	—18.6	0.069	0.0453	0.0867	0.015	0.050
Southern French type (63 samples)—													
Maximum ..	0.9988	22.18	17.60	0.918	1.4 : 100	0.656	4.56	—3.4	0.936	—	0.3162	0.045	0.290
Minimum ..	0.9882	8.07	6.40	0.318	3.4 : 100	0.219	1.09	—0.1	0.069	—	0.0988	0.034	0.148
Port type (50 samples)—													
Maximum ..	1.0429	22.19	17.61	0.707	4.5 : 100	0.700	17.22	—27.1	13.559	0.1861	0.9379	1.066	0.394
Minimum ..	0.9875	10.38	8.24	0.163	1.1 : 100	0.181	2.43	—1.4	0.228	0.0594	0.1893	0.059	0.222
Sherry and Madeira type (66 samples) —													
Maximum ..	1.0560	21.85	17.34	0.936	6.8 : 100	0.798	19.66	—23.1	17.210	0.1196	0.4751	0.350	0.436
Minimum ..	0.9866	8.22	6.52	0.324	2 : 100	0.253	1.31	—0.5	0.119	0.0504	0.0859	0.021	0.156

The must is fermented either by the addition of a special type of yeast or by the yeast occurring by accident on the grapes. According to the type of yeast doing the fermenting, rate of fermentation, and temperature various amounts of the following are produced:—Ethyl alcohol, glycerin acetic acid, aldehydes, volatile ethers, fixed ethers, succinic acid, and probably traces of the higher boiling alcohols—propyl, butyl, and amyl. These products of fermentation, the organic acids in the fruit, the mineral salts, colouring matter from the skins, and a large bulk of water form the wine.

Typical analyses due to König, of German, French, Austrian, Russian, Italian, and Spanish wines are given in Table I.

The following standards have been adopted by the United States:—"Wine is the product made by the normal alcoholic fermentation of the juice of sound ripe grapes and usual cellar treatment, and contains not less than 7 nor more than 16 per cent alcohol by volume, and in 100 cc. (20° C.) not more than 0.1 gm. of sodium chloride nor more than 0.2 gm. of potassium sulphate, and for red wine not more than 0.14 gm. and for white wine not more than 0.12 gm. of volatile acids produced by fermentation and calculated as acetic acid. Red wine is wine containing the red colouring matter of the skins of grapes. White wine is made from white grapes or the expressed juice of other grapes.

"Dry wine is wine in which the fermentation of the sugars is practically complete, and which contains, in 100 cc. (20° C.) less than 1 gm. of sugars, and for dry red wine not less than 0.16 gm. of grape ash and not less than 1.6 gm. of sugar-free grape solids, and for dry white wine not less than 0.13 gm. of grape ash, and not less than 1.4 gm. of sugar-free grape solids.

"Fortified dry wine is dry wine to which brandy has been added, but which conforms in all other particulars to the standard of dry wine.

"Sweet wine is wine in which the alcoholic fermentation has been arrested, and which contains in 100 cc. (20° C.) not less than 1 gm. of sugars, and for sweet red wine not less than 0.13 gm. of grape ash."

Fortified sweet wine is sweet wine to which wine spirits have been added. By Act of Congress "sweet wine" used for making fortified sweet wine and "wine spirits" used for such fortification are defined as follows:—"Wine spirits is the product resulting from the distillation of fermented grape juice to which water may have been added prior to, during, or after fermentation for the sole purpose of facilitating the fermentation and economical distillation thereof, and shall be held to include the products from grapes or their residues commonly known as grape brandy, and the pure sweet wine, which may be fortified free of tax, as provided in said section, is fermented grape juice only, and shall contain no other substance whatever introduced before, at the time of, or after

fermentation except as herein expressly provided, and such sweet wine shall contain not less than 4 per cent of saccharine matter, which saccharine strength may be determined by testing with Balling's saccharometer or must scale, and such sweet wine, after the evaporation of the spirits contained therein, and restoring the sample tested to original volume by addition of water. Provided that the addition of pure boiled or condensed grape must, or pure crystallised cane or beet sugar, or pure anhydrous sugar, to the grape juice aforesaid or the fermentation product of such grape juice prior to the fortification provided by this Act, for the sole purpose of perfecting sweet wine according to commercial standard, or the addition of water in such quantities as may be necessary in the mechanical operation of grape conveyors, crushers, and pipes leading to fermenting tanks, shall not be included by the definition of pure sweet wine aforesaid. Provided, however, that the cane or beet sugar, or pure anhydrous sugar or water so used, shall not, in either case, be in excess of 10 per cent of the weight of the wine to be fortified under the Act. And provided, further, that the addition of water herein authorised shall be under such regulations and limitations as the Commissioner of Internal Revenue, with the approval of the Secretary of the Treasury, may from time to time prescribe; but in no case shall such wines to which water has been added be eligible for fortification under the provisions of this Act where the same, after fermentation and before fortification, have an alcoholic strength of less than 5 per cent of their volume.

"Sparkling wine is wine in which the after part of the fermentation is completed in the bottle, the sediment being disgorged and its place supplied by wine or sugar liquor, and which contains in 100 cc. (20° C.) not less than 0.12 grm. of grape ash.

"Modified wine, ameliorated wine, corrected wine, is the product made by the alcoholic fermentation with the usual cellar treatment of a mixture of the juice of sound ripe grapes with sugar (sucrose) or a syrup containing not less than 65 per cent of sugar (sucrose) and in quantity not more than enough to raise the alcoholic strength after fermentation to 11 per cent by volume.

"Raisin wine is the product made by the alcoholic fermentation of an infusion of dried or evaporated grapes, or of a mixture of such infusion, or of raisins with grape juice."

Table II. is a list of American wines analysed by Bigelow.

Grape wine is adulterated in many ways: by watering, by addition of alcohol, by addition of excessive amounts of sugar or glucose, by coal-tar and vegetable colours, by antiseptics, by flavouring compounds, by using apple stock as the basis, and by "plastering."

Watering of wine, unless excessively done, is very difficult to detect, due to the varying composition of the grapes. Large amounts, of course, would abnormally lower the alcohol, extract, ash, acidity, and nearly all the constants. Gautier in his "Traité sur la Sophistication et l'Analyse des Vins" claims that the sum of the weight in grms. of alcohol in 100 cc. and the total acidity, expressed in grms. of sulphuric acid per litre, varies rarely below 13 or or above 17. Added water therefore would be indicated if the sum of the constants was reduced below 13.

A relation existing between the weight of the extract and that of alcohol was submitted in France by a committee whose duty it was to report on the addition of alcohol to wine. If the weight of the alcohol divided by the weight of the extract (both expressed in grms. per 100 cc.) exceeds 4.6 for red wines, the addition of alcohol may be strongly suspected, while in the case of white wines this quotient should not exceed 6.6.

It is frequently important to know the nature and the amount of sugar present in wine. This information is arrived at by making the direct and invert polarisation of the wine, and by running a determination for reducing sugars.

The polarisation of pure wine is nearly always left-handed unless, of course, all the sugar is fermented, and

then the reading will be zero. This is due to the dextrose being more fermentable than the lævulose. If commercial glucose or cane sugar has been added to a wine a sharp right-handed polarisation is found. If, after inversion, right-handed polarisation is still found, this indicates glucose. If the inversion changes the right-handed reading to left, cane sugar has been added.

Many colours are used to colour wine. The principal ones are fuchsin, acid fuchsin, and cochineal.

The antiseptics are used as preservatives. Boric and salicylic are normal in some wines, and their detection should be quantitative. Sulphurous acid should also be quantitative.

Flavouring principles, as elderberry flowers, bitter almonds, &c., are used very often in composition wines to duplicate various well known brands.

Apple stock is very often used as the basis to make wine. This is then flavoured, coloured, and by addition of sugar allowed to ferment. This spurious grape wine may be detected by a flame test. The potash flame is readily seen when apple stock has been used, while in a pure grape wine the sodium flame predominates.

By "plastering" is meant the addition of calcium sulphate (plaster of paris) to the must before fermentation. This practice is in vogue in France, Italy, and Spain. The CaSO_4 reacts with the potassium bitartrate present in grape wine. It is claimed that this clarifies the wine by carrying down mechanically impurities, increases solubility of the colouring matter, aids fermentation by making it more rapid and complete, and enhances keeping qualities. The effects of plastering increases the ash, and is, in some countries, forbidden.

(To be continued).

MEETINGS FOR THE WEEK.

TUESDAY, Feb. 1st.—Royal Institution, 3. "The Physiology of Anger and Fear," by Prof. C. S. Sherrington.

— Röntgen Society, 8.15. Discussion on "The Injurious Effects produced by X-rays," opened by Dr. Sidney Russ. Demonstration of Lantern Slides obtained in Gallipoli, by Dr. Herschell Harris.

WEDNESDAY, 2nd.—Royal Society of Arts, 4.30. "Women's Work during and after the War," by The Hon. Lady Parsons.

— Society of Public Analysts, 8. (Annual General Meeting). "Human Milk," by G. D. Elsdon. "Common Processes used in Water Analysis," by W. T. Burgess. "Poll Oil—a New Adulterant of Ghee," by J. H. Parnes and Arjan Singh.

THURSDAY, 3rd.—Royal Institution, 3. "The Utilisation of Energy from Coal—Industrial Applications of Gaseous Fuels derived from Coal," by Prof. W. A. Bone.

— Royal Society. "An Orderly Dissimilarity in Inheritance from different Parts of a Plant," by W. Bateson and C. Pellieu. "Observations on Coprozoic Flagellates, together with a Suggestion as to the Significance of the Kinetocyt-nucleus in the Binucleate," by H. M. Woodcock. "Investigations dealing with the Phenomena of Clot Formation—Part III., Further Investigations of the Cholate Gel," by S. B. Schryver. "Mechanism of Chemical Temperature Regulation," by J. M. O'Connor.

— Chemical, 8. "The Recent Work on X-rays and Crystals and its Bearing on Chemistry," by Prof. Bragg.

FRIDAY, 4th.—Royal Institution, 5.30. "Fifteen Years of Mendelism," by Prof. W. Bateson.

SATURDAY, 5th.—Royal Institution, 3. "The Shakespeare Tercentenary—The Range of Shakespeare's Influence," by Sir Sidney Lee.

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THE CHEMICAL NEWS.

VOL. CXIII., No. 2932.

THE PERMANGANATE AND IODIMETRIC DETERMINATION OF IODIDE IN PRESENCE OF CHLORIDE AND BROMIDE.*

By O. L. BARNEBEY.

(Concluded from p. 44).

2. The Iodimetric Titration of Iodate formed by the Permanganate Oxidation.

DURING the study of the permanganate titration of iodides potassium iodide was added in a number of instances to the solution after the final titration of the excess of ferrous sulphate with permanganate and the resulting iodine titrated with standard thiosulphate. The results obtained were surprisingly accurate; consequently the author decided to study the factors influencing this titration.

The first point of interest is naturally the effect of ferric iron on potassium iodide in the acid medium necessary for the liberation of iodine by the interaction of iodic and hydriodic acids.

Tenth-normal potassium iodate (3.5678 grms. pure KIO_3 per litre), ferric chloride (1 cc. = 0.006374 gm. Fe) slightly acid with hydrochloric acid, ferrous sulphate solution (1 cc. = 0.004528 gm. Fe) slightly acid with sulphuric acid, 5/N hydrochloric acid, 10/N sulphuric acid, 10/N phosphoric acid (computed on basis of three replaceable hydrogen atoms), manganese preventive solution containing 200 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 340 cc. H_3PO_4 (sp. gr. 1.7) per litre, N potassium iodide, and 0.1055/N sodium thiosulphate were used in the experiments of Table V. The letter s designates the experiments in which starch was used as indicator. When starch was not used the bleaching of the iodine colour of the solution was taken as the end-point.

This series (Experiment 2) shows that normal phosphoric acid is capable of decreasing the speed of reaction between over a tenth of a gram. of ferric iron and 0.05/N potassium iodide in a volume of 100 cc. at room temperature (21°) to such an extent that it becomes negligible for one or two minutes, only amounting to 0.04 cc. of 0.1/N thiosulphate in ten minutes. A considerable increase of the concentration of phosphoric acid, even to 4/N, does not change the speed of reaction sufficiently to give a measurable difference of volume of thiosulphate required by the method employed. Dilution of the normal solution to 400 cc. (Experiment 8), thus diminishing the concentration of all the reagents involved, causes a still lower rate of reaction. Sulphuric acid (Experiments 9 and 10) can not be substituted for phosphoric acid, since its action toward decreasing the rate of reaction is not commensurate with the latter. The preventive solution containing phosphoric acid (Experiments 11 to 15) employed in the permanganate determination of iodides exerts the same influence as phosphoric acid itself. Experiment 16 shows that ferrous iron is without effect. Experiments 18 to 22 show that iodic acid can be titrated quantitatively in the presence of the phosphoric acid or preventive solution, and Experiments 23 and 24 show that the ferric chloride has no influence on the titration of iodic acid if the titration is performed immediately after adding the potassium iodide.

Definite samples of potassium iodide were taken in the Series VI., and varied quantities of potassium bromide and sodium chloride added to each, after which the sample was analysed for iodine by the permanganate method as previously outlined and the result recorded. Ferrous sul-

phate solution was then added in slight excess, followed by 5 cc. of N KI, and the free iodine titrated immediately with standard thiosulphate, adding 1 cc. of 1 per cent starch solution when the solution became very faintly yellow, in order to get the sharp iodine-starch end-point. The permanganate, ferrous sulphate, and thiosulphate solutions used in this series were tenth-normal and the potassium iodide was hundredth-normal.

Table VII. includes results obtained using 0.001/N solutions. The 0.001/N KMnO_4 is thousandth-normal compared with KI as standard. Reacting with iron in acid solution this permanganate would be 0.01/N, inasmuch as 2KMnO_4 or $\text{K}_2\text{Mn}_2\text{O}_8$ will react with 10 Fe in acid solution, but will only oxidise one molecule of KI to KIO_3 in alkaline solution. Hence the permanganate contains 0.316 gm. of potassium permanganate per litre. The same relative strength obtains for the ferrous sulphate solution used in this series. The thiosulphate solutions used in this work were standardised against pure potassium iodate, referring the normality strength of the thiosulphate (0.001/N) to potassium iodide as a basis rather than to the iodate. The same precautions used in Series IV. are necessary here to avoid any slight impurities of oxidising or reducing character in the permanganate determination. The manganese solution used in these two series contained 200 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ + 350 cc. of H_3PO_4 (sp. gr. 1.7). In Table VI. 15 cc. and in Table VII. 5 cc. of this solution were added in each experiment.

TABLE VI.—Iodimetric Determination of Iodide in Halide Mixtures,

Present (grm.).		Total volume. C.c.	KI (grm.).		
KBr.	NaCl.		Present.	Found by KMnO_4 .	Found by $\text{Na}_2\text{S}_2\text{O}_3$.
1. 0.5953	0.5851	300	0.0830	0.0828	0.0827
2. 0.5953	0.5851	300	0.0830	0.0827	0.0826
3. 0.5953	0.5851	300	0.0830	0.0829	0.0826
4. 0.5953	0.5851	300	0.0415	0.0414	0.0415
5. 0.5953	0.5851	250	0.0415	0.0412	0.0415
6. 0.5953	0.5851	200	0.0166	0.0168	0.0165
7. 0.5953	0.5851	200	0.0083	0.0082	0.0080
8. 0.5953	0.5851	200	0.0017	0.0018	0.0016

TABLE VII.—Iodimetric Determination of small amounts of Iodide in Halide Mixtures.

1. 0.0595	0.0585	200	0.00830	0.00825	0.00825
2. 0.0595	0.0585	200	0.00830	0.00832	0.00826
3. 0.0595	0.0585	100	0.00415	—	0.00414
4. 0.0595	0.0585	100	0.00166	0.00169	0.00170
5. 0.0238	0.0234	100	0.00083	0.00084	0.00085
6. 0.0238	0.0234	100	0.00033	0.00033	0.00033
7. 0.0119	0.0117	100	0.00017	0.00017	0.00017

These two series show that the iodimetric titration of the iodate in the residual solution from the permanganate method is accurate if the solution contains sufficient phosphoric acid to prevent the action of ferric iron on potassium iodide. Naturally if the permanganate data are not desired they can be neglected and only the thiosulphate titration computed. The iodimetric method is to be preferred when titrating such small amounts of iodine as the samples of Series VII. contained, essentially because of the sharpness of the starch-iodine end-point contrasted with that of permanganate, and of the lesser effect of slight impurities such as oxygen in water on the final titration with the thiosulphate.

The following procedure is well adapted to the analysis of a halogen mixture for its iodine content. 1-20th to 5 grms. of sample, depending upon the amount of iodine present, is dissolved in 100 cc. of recently boiled distilled water in an Erlenmeyer flask, 1 cc. of N sodium hydroxide added; the solution is heated to boiling and standard permanganate added, 5 to 10 cc. at a time, with continuous shaking, allowing several seconds between each addition before observing the colour of the solution. (Note.—If as small a sample as 0.05 gm. is desired a larger portion

* Journal of the American Chemical Society, xxxvii., No. 6.

TABLE V.—Reaction between Ferric Iron and Potassium Iodide in Sulphuric and Phosphoric Acid Solutions.

 $\text{FeCl}_3 = 0.006374$ gram. Fe per cc. $\text{FeSO}_4 = 0.004528$ gram. Fe per cc. $\text{Na}_2\text{S}_2\text{O}_3 = 0.1055/\text{N}.$

5 cc. of normal KI solution used in each experiment.

	FeCl ₃ . Cc.	FeSO ₄ . Cc.	0.1/N KIO ₃ . Cc.	Normality.			Mn preventive solution. Cc.	Volume. Cc.	Na ₂ S ₂ O ₃ . Cc.	Time. Minutes.
				H ₃ PO ₄ .	H ₂ SO ₄ .	HCl.				
1.	20	—	—	0.5	—	—	—	100	0.10 s	10
2.	20	—	—	1.0	—	—	—	100	0.04 s	10
3.	20	—	—	2.0	—	—	—	100	0.04 s	10
4.	20	—	—	2.0	—	—	—	100	0.04	10
5.	20	—	—	0.25	—	—	—	200	0.04 s	10
6.	20	—	—	0.125	—	—	—	400	0.04 s	20
7.	20	—	—	0.5	—	—	—	200	0.04 s	20
8.	20	—	—	0.25	—	—	—	400	0.04 s	34 (b)
9.	20	—	—	—	1.0	—	—	100	5.00	2
10.	20	—	—	—	0.25	—	—	400	4.50 s	20
11.	20	—	—	—	—	—	5	100	0.04 s	10
12.	20	—	—	—	—	—	10	100	0.04 s	10
13.	20	—	—	—	—	—	5	200	0.04 s	10
14.	20	—	—	—	—	—	5	400	0.04 s	55 (b)
15.	20	—	—	—	—	—	10	400	0.04 s	72 (b)
16.	—	50	—	—	—	—	10	200	0.00 s	60
17.	—	50 (a)	—	—	—	—	10	200	0.04 s	10
18.	—	—	30	—	—	—	10	200	28.44 s	Immediately
19.	—	—	50	—	—	—	10	200	47.44 s	"
20.	—	—	30	5.0	—	—	—	200	28.44 s	"
21.	—	—	30	—	—	5	—	200	28.46 s	"
22.	—	—	30	—	—	—	5	200	28.44 s	"
23.	20	—	30	—	—	—	5	200	28.46 s	"
24.	20	—	30	—	—	—	10	200	28.44 s	"

(a) Oxidised with permanganate, then 1 cc. of ferrous sulphate was added in excess.

(b) At the end of twenty minutes starch solution was added and a drop of thiosulphate (0.04 cc.), and the remainder of the time was required for a very faint blue colour to reappear.

should be weighed out and an aliquot analysed; for example, 0.5 gram. diluted to 500 cc. and a 50 cc. portion used in the analysis). If the solution becomes cooled it is reheated and the additions are continued until a distinct colour (red or green) is imparted to the solution. The flask is covered with a small watch-glass and the liquid then heated just below boiling for about five minutes. If the colour disappears more permanganate is added and the solution reheated. It is then cooled in running water, and to it is added, all at once, with agitation of the solution, a mixture of 15 cc. of manganese preventive solution (200 grms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O} + 350$ cc. H_3PO_4 , of sp. gr. 1.7 per litre) and sufficient standard ferrous sulphate to react with all the manganese dioxide and excess of permanganate, and have an excess of 10 to 15 cc. As soon as the manganese dioxide has dissolved completely the solution is diluted to 300–400 cc. and titrated with the permanganate to the first appearance of a faint pink colour. A smaller amount of preventive solution can be added and a smaller volume used with small quantities of iodine involved. The percentage of iodine is calculated from the amount of permanganate required to oxidise the iodide to iodate.

(Note.—No iodide colour should be visible before titration with permanganate or before the addition of potassium iodide prior to the thiosulphate titration. If such a colour develops the proper adjustment has not been made between an exceptionally high concentration of ferric iron and phosphoric acid, or too long a time has intervened between the time of finishing the permanganate and starting the thiosulphate titration, in which case another sample must be analysed, using a greater dilution and correspondingly more preventive solution or phosphoric acid).

For the iodimetric titration a few drops of ferrous sulphate are added to bleach out any excess of permanganate,

followed by 5 cc. of N KI solution (free from iodine) or 1 gram. of solid, after which the iodine is titrated immediately with standard thiosulphate. The percentage of iodine or iodide is then computed from the amount of thiosulphate required to react with the iodine produced by the reduction of the iodate to iodide.

The two methods have about equal merit except when applied to extremely small quantities of iodides, when the iodimetric method is preferable. If the iodimetric method only is to be followed, naturally the strength of the permanganate and ferrous sulphate solutions need not be known exactly.

Summary.

1 In the original method of Pean de St. Gilles for titrating iodide in the presence of bromide and chloride with permanganate, the results are erroneous because of the formation of free bromine, chlorine, or hypochlorous acid.

2. The presence of manganese sulphate and phosphoric acid in the ferrous solution allows the removal of the excess of permanganate and manganese dioxide without liberation of bromine or chlorine from the halides. Likewise the manganese and phosphoric acid ensure a correct permanganate titration of the ferrous iron excess.

3. Iodide can also be determined in the presence of bromide and chloride by addition of potassium iodide to the final solution obtained as in 2, and titration of the liberated iodine with thiosulphate.

4. Both titrations can be made on a single sample, using the residual solution from the permanganate titration for the iodimetric determination.

Very small amounts of iodine are best determined by the iodimetric method. With moderate quantities of iodine both methods outlined are easy of manipulation, rapid in execution, and accurate.

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WINE ANALYSIS.*

(Concluded from p. 8).

In judging the purity of a wine the following determinations are most valuable: Alcohol, extract, glycerol, ash, total and volatile acids, reducing sugar, coloring matter, and preservatives.

The actual percentage of the above is not so important as the relation between them, such as alcohol to glycerol, alcohol to acids, and volatile acids to total acids.

1. Specific Gravity.

Determine at 15° C. by means of a pycnometer, Westphal balance, or a small, accurately graduated hydrometer.

2. Alcohol.

Place 100 cc. of the wine at 15° C. and 50 cc. of water in a distillation flask of about 300 cc. capacity. Attach the flask to a vertical condenser and distil almost 100 cc., making up to 100 cc. at 15° C. If foaming occurs add a small amount of tannin. If acetic acid fermentation has set in strongly add 0.1 to 0.2 gm. of precipitated calcium carbonate. Determine the specific gravity of the distillate as under 1, and obtain corresponding percentage of alcohol by volume and gm. per 100 cc. from tables in Leach, Government bulletins, or

some chemical handbook. The weight of the distillate times the per cent of alcohol divided by the weight of the sample equals the per cent of alcohol by weight.

3. Extract.

(a) *In Dry Wine*.—Evaporate 50 cc. of the sample on the water-bath to a syrupy consistency in a flat-bottomed platinum dish approximately 85 mm. in diameter and of about 75 cc. capacity. Heat the residue for two and one-half hours in a drying oven at the temperature of boiling water, and weigh. The sugar free extract is found by deducting the weight of sugar in excess of 0.1 gm. per 100 cc. from the total residue. In the case of plastered wines, the potassium sulphate in excess of 0.1 gm. is also deducted.

(b) *In Sweet Wines*.—When the extract content is between 3 and 6 grms. per 100 cc. treat 25 cc. of the sample as described under (a) of dry wines. If the extract exceeds 6 grms. per 100 cc. the approximate determination of the extract is made by consulting tables compiled by Windisch. A measured portion of wine is evaporated on water-bath to one-fourth its volume, and then diluted with H₂O exactly to volume measured. The specific gravity of this dealcoholised liquid is determined at 15° C., and from Windisch tables the corresponding extract for the specific gravity is read off. This latter method must be used due to the serious error involved with drying levulose at high temperature. Windisch tables are in Leach, *Bull.* 107, and books on wine analysis.

4. Glycerol.

(a) *In Dry Wines*.—100 cc. of the wine are evaporated on the water-bath to a volume of about 10 cc.; one or two grms. of fine sand are added, and sufficient milk of lime added to make alkaline. Continue evaporation nearly to dryness, cool, and shake with 50 cc. of 95 per cent alcohol; heat to boiling on the water-bath and filter. The insoluble residue is washed on the filter-paper with several portions of hot alcohol, using about 100 cc., and the washings added to the original filtrate. The alcoholic filtrate is evaporated to a syrupy consistency on the water-bath. This residue is then dissolved in 10 cc. of absolute alcohol and transferred to a flask with 15 cc. of ether. The flask is tightly corked, shaken, and allowed to stand for some time. Filter into a tared dish, wash with a mixture of absolute alcohol (1 part) and ether (1.5 parts); evaporate the filtrate to a syrupy consistency on the water-bath, dry in a water oven for one hour, and weigh as glycerin.

With plastered wines the results are too high because of the potassium sulphate that is present and decomposed by the lime to form potassium hydroxide, which is soluble in glycerin and alcohol. In plastered wines the above residue should be ignited and the ash deducted from the above weight.

(b) *Sweet Wines*.—In the case of sweet wines, containing more than 5 per cent of sugar, only 50 cc. of the wine are used for the estimation of the glycerin. The sand and lime are added and the mixture warmed on the water-bath. After cooling treat with 100 cc. of 95 per cent alcohol, allow the precipitate formed to settle, filter, and wash the insoluble matter with spirit. The alcoholic filtrate obtained is then treated as above described.

Glycerol-Alcohol Ratio.

Express this ratio: X:100, in which X is obtained by multiplying the per cent by weight of glycerol by 100 and dividing the result by the percentage by weight of alcohol.

5. Determination of Potassium Sulphate.

100 cc. of the sample is acidified with hydrochloric acid heated to boiling and an excess of barium chloride solution added. Filter, wash, dry, ignite, and weigh as barium sulphate. Calculate the equivalent of potassium sulphate.

* Methods of Analysis used in the Laboratories of the Armour Institute of Technology. From the *Chemical Engineer*, xli., No. 2.

If more than 0.06 grm. per 100 cc. is present, plastering is indicated.

6. Ash.

Weigh 2 grms. of the extract dried, and burn until free from carbon at the lowest possible heat.

7. Ash-Extract Ratio.

Express results as 1 : X, in which X is the quotient obtained by dividing the percentage of extract by the percentage of ash.

8. Total Acidity.

In carbonated liquors the carbon dioxide is first expelled by pouring the wine back and forth from one beaker to another, and from time to time removing the excess froth on top of the vessel by aid of the hand. 25 cc. of the sample is taken and heated just to the boiling point, and then titrated with tenth normal sodium hydroxide, using in the case of white wine phenolphthalein as an indicator. With red wine delicate litmus paper should be used. Total acidity is calculated as tartaric acid. Each cc. N/10 alkali corresponds to 0.0075 grm. tartaric acid.

9. Volatile Acids.

The volatile acid is expressed as acetic. 50 cc. of the wine and a little tannic acid are transferred to a distilling flask, the stopper of which is provided with two tubes. One leads to a flask containing about 300 cc. water, and the other tube connects to a distilling flask. Contents of both flasks are brought to boiling. The flame of distilling flask is lowered, and a flow of steam is sent through the distilling flask from the water flask until about 200 cc. of distillate is collected in a receiving flask. This distillate is titrated with N/10 NaOH, phenolphthalein as indicator. Each cc. of N/10 NaOH is equivalent to 0.006 grm. acetic acid.

10. Fixed Acids.

Determine by difference of the total acidity and volatile acids. The volatile acids being calculated for purpose of subtraction in terms of tartaric acid or other acid that total acidity is expressed in.

11. Detection of Free Tartaric Acid—Nessler's Method.

A small portion of wine is shaken at intervals in a corked flask with some powdered cream of tartar. The liquid is then filtered, and to the filtrate a little 20 per cent potassium acetate solution is added. The liquid is stirred, and if any free tartaric acid is present there will be a precipitate of cream of tartar. If no precipitate, let stand awhile and examine again.

12. Total Tartaric Acid.

2 cc. of glacial acetic, 15 grms. of powdered potassium chloride, and 3 drops of a 20 per cent solution of potassium acetate are added to 100 cc. of wine. This mixture is then stirred to hasten the solution. 15 cc. of 95 per cent alcohol is added, and the side of beaker is rubbed vigorously with a glass rod to start crystallisation. Allow to stand fifteen hours at room temperature; decant through a gooch with a thin film of asbestos. Do this rapidly, and allow no more of the acid potassium tartrate to be transferred on the gooch than possible. The precipitate is then washed three times with a small amount of a mixture of 15 grms. potassium chloride, 20 cc. of 95 per cent alcohol, and 100 cc. of H₂O, using no more than 20 cc. of the wash solution in all. Transfer the asbestos film and precipitate to the beaker in which the precipitation took place, wash out the gooch with hot water and add 50 cc. of hot water, heat to boiling, and titrate the hot solution with decinormal sodium hydroxide, using delicate litmus tincture or litmus paper as indicator. Increase the number of cc. of decinormal alkali employed by 1.5 on account of the solubility of the precipitate. This figure multiplied by 0.015 gives the amount of total tartaric acid in grms. per 100 cc.

13. Cream of Tartar.

Ignite the residue obtained from the evaporation of 50 cc. of wine as directed under ash determination. Exhaust the ash with hot water, add to the filtrate 25 cc. of decinormal hydrochloric acid, heat to incipient boiling, and titrate with decinormal alkali solution, using litmus for an indicator. Deduct from 25 cc. the number of cc. of N/10 alkali employed, and multiply the remainder by 0.0188 for potassium bitartrate expressed in grms.

14. Free Tartaric Acid.

Ash 50 cc. of wine. Add 25 cc. of N/10 HCl, heat to incipient boiling and titrate with N/10 NaOH, using litmus as indicator. Deduct the number of cc. employed from 25 and multiply the remainder by 0.0075 to obtain the amount of tartaric acid necessary to combine with all the ash (considering it to consist entirely of potash). Deduct the figure so obtained from the total tartaric acid for the free tartaric acid.

15. Reducing Sugar.

Determine as dextrose by Defreuz or the Allihn method. For this purpose dilute a measured portion of the wine and evaporate on the water-bath to one-fourth its original volume. Clarify with sub-acetate of lead, and add enough water so that solution contains one-half of 1 per cent of sugar for the Defreuz and about 1 per cent of sugar for the Allihn method. One may assume 2 per cent as the sugar free extract of wine, the number of volumes of water to be added to the filtrate being determined by the difference between 2 and the total extract as determined.

16. Tannin.

A method by Nessler and Barth is an approximate one for determining tannin. To 12 cc. of wine add 30 cc. of alcohol and filter. Evaporate 35 cc. of the filter, which corresponds to 10 cc. of wine, to about 6 cc., and transfer to a 10 cc. graduated centrifugal tube. Add a few drops of 40 per cent sodium acetate and a slight excess of 10 per cent ferric chloride. The tube is corked, gently agitated, and allowed to stand twenty-four hours. Then measure the volume of precipitate. Each cc. of precipitate is equivalent to 0.033 per cent of tannin in the wine.

17. Foreign Colours in Wine.

Colours most commonly found in wine are cochineal, fuchsin, and acid fuchsin.

The "Pharmacopœia" gives the following colour tests:—

If 2 cc. of red wine are mixed in a test-tube with 2 drops of chloroform and 4 cc. of normal potassium hydroxide, and the mixture carefully heated, the disagreeable odour of isonitril should not become perceptible (absence of various aniline colours).

If 50 cc. of red wine be treated with a slight excess of ammonia water the liquid should acquire a green or brownish green colour; if it be then well shaken with 25 cc. of ether, the greater portion of the ethereal layer removed, and evaporated in a porcelain capsule with an excess of acetic acid and a few fibres of uncoloured silk, the latter should not acquire a crimson or violet colour (absence of fuchsin).

If 25 cc. of red wine, heated to about 45° C., be well agitated with 25 grms. of manganese dioxide, the liquid filtered off and acidulated with hydrochloric acid, it should not acquire a red colour (absence of sulphofuchsin).

Dupres Method of Detection.

Small cubes of jelly, measuring about 2 cm. in thickness, are prepared as follows:—Dissolve 1 part pure gelatin in 10 parts boiling water, and pour upon a plate to harden. This is then cut into cubes, as mentioned above. A suspected wine is treated by immersing one of these cubes therein for twenty-four hours, after which it is removed and washed slightly in cold water and cut through with a knife. If the colour is a natural one it will lightly tinge

the outer surface of the cube but will not permeate far below the surface, so that the inner portion of the cross section will be largely free from colour. Nearly all foreign colouring matter used in wine, such as most coal-tar dyes, cochineal, Brazil wood, logwood, &c., will be found to deeply permeate the jelly cube, often to the centre. Information as to the nature of the colour may sometimes be gained by immersing the dyed jelly cube in weak ammonia. If the colour be rosanilin the cube is decolorised; if cochineal, a purple coloration will result, and if logwood, a brown tinge.

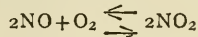
FIXATION OF ATMOSPHERIC NITROGEN.*

By LELAND L. SUMMERS.

(Concluded from p. 45).

III. Description of Processes (continued).

Method of Utilising NO.—All of the above nitric acid processes utilise the reaction—



which is an exothermic one for the formation of the peroxide, and if the temperatures are controlled, side reactions can be prevented and equilibrium can be maintained with only a small percentage of NO remaining. The gases, after leaving the furnaces, are usually carried through waste heat boilers where 50 to 60 per cent of the heat is utilised for steam production. They are then cooled in aluminium pipe coolers, and allowed to enter a gas holder, where time is given to form the peroxide. The products then enter counter current absorption towers, where the reaction with water forms $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2$. The nitrous acid, HNO_2 , is further oxidised and utilised to form HNO_3 in contact with the excess oxygen in the gases and with the absorbing water. The final recovery is usually made by circulating the gases through two towers of weak alkaline solution, such as sodium carbonate, and this is converted into sodium nitrate and into sodium nitrite, and recovered by evaporation; the final products are a combined nitrate-nitrite of sodium. A normal circulation over three absorbing towers gives an acid of about 30 per cent concentration, but this can be increased to 45 to 50 per cent by re-circulating over the first tower. Further concentrations are usually made by evaporation. All of these processes are simplified by increased concentrations of NO in the initial reaction. About 2 to 3 per cent of the original NO is discharged in the waste gases from the absorbing towers. It will be noted that one great advantage of these processes is that they require the handling of only air, gas, and water up to the time the nitric acid is formed in the absorbing towers, so that the simplest handling devices suffice and the labour is a minimum; also no chemicals are required until the final washing with the alkaline solution in the absorbing towers, and this may be a cheap solution, such as lime-water, if conditions make it desirable.

Cyanamide Process.—The very low yields, representing less than 5 per cent of the energy expended, and amounting to 65 kw.-hr. per kg. of N fixed, naturally have turned attention to chemical reactions as a means of increasing the yields. One of the most important of these is the process for making cyanamide, CaCN_2 . As a separate paper is to be presented here covering this subject, we will only generalise.

The endothermic reaction and the heating of the materials entering into the calcium carbide reaction have an approximate theoretical value of 3.1 kw. hr. per kg. produced, whereas it requires about 4 kw.-hr. to produce a kg. of 85 per cent calcium carbide in the best practice.

For 100 per cent carbide it would require 4.7 kw.-hr., and the efficiency is therefore—

$$\frac{3.1}{4.7} = 66 \text{ per cent.}$$

The union of carbide and nitrogen is exothermic when a sufficient temperature is reached, so the actual expenditure of energy for this reaction is not in excess of 0.1 to 0.2 kw.-hr. additional for the fixation of the nitrogen. We require, further, the preparation of the nitrogen and the grinding of the carbide to prepare it for the nitrogen treatment. The cyanamide can be used directly in the fertiliser industry, but for use in the chemical industries it must be decomposed to form ammonia; or, if nitric acid is required, it must be made from the ammonia by some process such as the Ostwald contact process. We may figure, however, that the yield for a given amount of

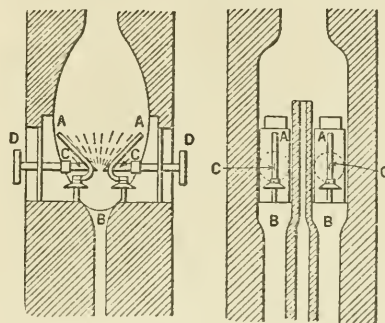


FIG. 4.—PAULING FURNACE.

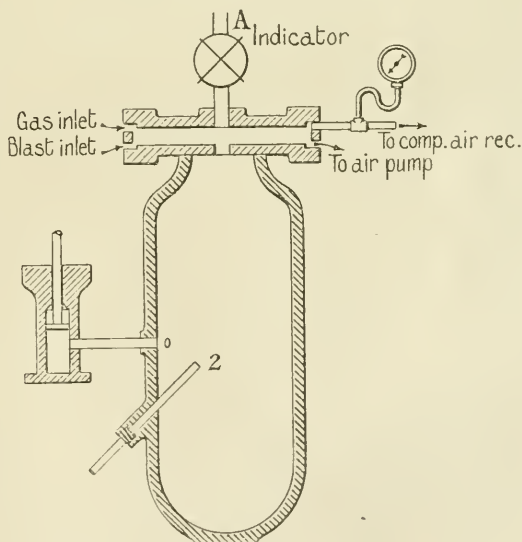


FIG. 5.—HAUSER PROCESS.

electric energy, which amounts to about 16.6 kw.-hr. per kg. of N fixed, is from four to five times the yield of the direct nitric acid processes, while offsetting this is the cost of preparing the nitrogen, the cost of chemicals, the handling of materials at high temperature, and the many factors making up manufacturing costs.

The Serpek Process.—The Serpek process is typical and has been quite extensively introduced commercially. The reaction is represented by the equation $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$. The reacting temperature for best results is claimed to be 1800° C. to 1900° C., but no effort is made to define the equilibrium conditions, and

* Paper presented at a joint meeting of the American Institute of Electrical Engineers and the New York Section of the American Electrochemical Society.—From the *Chemical Engineer*, xxi., No. 6.

it is very evident that where CO enters so actively into the reaction, the temperatures can be materially altered by a change in the partial pressures of the N and CO. One of the most interesting features of this process is that the impure Al_2O_3 in the form of bauxite is fed into the furnace together with coal, and the sensible heat is therefore partially derived from the coal. Neglecting the specific heats of the solids, the endothermic reaction requires 3 kw.-hr. per kg. of aluminium nitride having an approximate content of 26 to 34 per cent N; it would require therefore 9 to 10 kw.-hr. per kg. of N under the best conditions if the coal and producer were capable of supplying all the heat energy required to produce the required temperature in the gaseous and solid products. In the case of cyanamide it requires about 4 kg. of high-grade carbide per kg. of nitrogen, or a kg. of N requires 16 kw.-hr. under favourable conditions and about 0.2 kw.-hr. for heating the carbide against 10 to 12 kw.-hr. in the Serpek process. If all energy were supplied from the electric source the Serpek process would require practically the same electric energy as the cyanamide process.

There is a distinct advantage in being able to use producer gas in place of preparing purified nitrogen, and there is a further advantage in conducting the process with one operation. In practice Serpek uses a revolving barrel furnace of the resistance type, the resistance consisting of a squirrel-cage construction which continually agitates the material as it passes through. In all nitride reactions this is essential, as the materials become coated with a covering which protects the interior and prevents further absorption of nitrogen. Serpek feeds bauxite and coal from a producer type of furnace into this revolving electric furnace, and the sensible heat is thus utilised to heat the material as it travels to the electric furnace; the product is discharged from the electric furnace as aluminium nitride, with a content of 26 per cent to 34 per cent N.

The aluminium nitride can be treated with steam and the N converted into ammonia, or the ammonia may be converted into nitric acid. Serpek claims a process for converting the nitride directly into nitric acid, but no details are available. One drawback to using bauxite is that the resulting aluminium oxide is more difficult to use than the impure bauxite, and the process does not work as economically. It is probable that some cheap catalytic agents may be found to substitute for the bauxite, but otherwise the Serpek process should necessarily find its greatest application in connection with the reduction of aluminium.

Haber Catalytic Process.—One other process which has attracted marked attention on account of the scientific eminence of its inventor, as well as the commercial results obtained, is the Haber process for the synthesis of ammonia directly from its components N and H. This means that there must be a supply of these elements available, or they must be cheaply produced. The reaction is an exothermic one producing 11,000 calories per gm.-molecule, so the problem is not so much the energy consumption as the peculiarities of the reaction, $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$. The ammonia formed is practically decomposed at 750°C . It has been difficult to get any substance to react with the N at this low temperature, and, while the nitrogen was made active toward many substances, it was easy to decompose the resulting NH_3 into its constituent molecules, and all yields obtained were too low to justify commercial results. Haber's success seems due more to ingenuity in constructing his apparatus and to the discovery of a suitable catalyser than to any departure from previously known principles. The fact that one molecule of N and three of H form only two molecules of ammonia indicates that the volume occupied by the ammonia will occupy only one-half the space occupied by its constituent gases, and hence this contraction of volume will be assisted by pressure. Haber increased the pressure on the reacting gases to 200 atmospheres, and as a catalyser he used uranium. He found at 500°C , he could react on the nitrogen and upwards of 8 per cent of ammonia could be

formed before equilibrium took place. By using limited amounts of N and an excess of H the equilibrium pressures were adjusted well within the decomposition limits of temperatures, and by withdrawing the gases from the catalyser as they reached equilibrium the process was made continuous. The fact that decomposing ammonia creates a most destructive corrosive agent had to be met, and the retorts had to be made strong enough to stand the effects of the high pressure and also possible explosion, as hydrogen compressed to 200 atmospheres and heated to 500°C . is a most active agent in the presence of impurities such as oxygen, sulphur, &c. The retorts can be made of very moderate size and a number of them used, and by heating internally with electric resistance the shells are not subjected to the effects of temperature, so the process seems to have met with very pronounced technical success. The consumption of energy for heating the gases is very slight, as the exothermic reactions will compensate largely for the heat required to release this.

The preparation of the N and H and the compression to 200 atmospheres will represent the greatest costs of production. It will be noted that all products are handled in the gaseous condition, being most favourable for low labour costs. The ammonia is extracted from the mixture of N and H by slightly cooling the gases until the point of liquefaction of ammonia is reached, and the ammonia condenses out. The remaining gases are passed back to the retort without sacrificing the original pressure of compression. The work done on the gases is thus reduced to a minimum, and equilibrium can be continually disturbed by withdrawing the products without heavy losses. This process involves the expenditure of approximately 1.5 kw.-hr. per kg. of N, and therefore represents the lowest consumption of energy of any of fixation processes.

From an engineering point of view the various processes must be considered from other than the technical standpoint, the question of particular application being the guiding consideration in most cases.

IV.—The Economics of Nitrogen Fixation.

Fertilisers.—In considering nitrogen fixation and its relation to fertilisers we must remember it is only one of the three important ingredients of fertilisers, the other two being phosphorus and potassium. It is possible to obtain nitrogen from the atmosphere and transfer it to the soil by means of nitrifying bacteria, which may be cultivated by such plant life as the legumes, to which family belong the clover and alfalfa. These plants have a nodule on the stem which is the seat of the bacteria activity, and if the plants containing this nitrogen are returned to the soil, the soil may be enriched in nitrogen, but the crop must be sacrificed or partially so. When it is not desirable to plant these nitrifying crops, recourse must be had to nitrogen in the form of fertiliser. Unfortunately all crops deprive the soil of fertility, and in the case of phosphorus and potassium converted into the crops, these must actually be replaced or barren soil will eventually result. Each soil must be treated for the particular crop it is to bear, and usually there are fixed mixtures which become standard for various crops. These mixtures contain the nitrogen, the phosphorus, and the potassium in varying amounts. The output of nitrogen from a chemical works would ordinarily be shipped to these fertiliser manufacturers unless the chemical works desired to manufacture the mixed fertilisers.

Of all the processes we have considered, the cyanamide is the only one which manufactures a product which is in a form to go into the fertiliser market direct. The nitric acid processes must unite the acid with some alkaline base such as sodium, lime, or ammonia, and the ammonia process must unite the product with an acid such as sulphuric or nitric. The nitride processes can hardly afford to ship the nitride, as it is combined with an ore or base such as aluminium oxide, which may be more desirable in the aluminium industry, as the fertiliser industry will pay only on a nitrogen basis.

Price of Nitrogen.—In general the price of combined nitrogen, as we have seen, is fixed by the price of Chile nitrate. Thus if this sells for 2 cents per pound and contains 15 per cent N, the price per pound of N is 13.2 cents, and this in turn would make the price of ammonia sulphate, having 21 per cent of nitrogen, 2.7 cents per pound. These have been current prices. In considering the production of nitrogen products, it would seem that, while these prices control nitrogen for the fertiliser industry, it would be desirable to produce if possible products which are manufactured from these crude products, and thus avoid competition with the natural products direct. Nitric acid of commerce is manufactured from soda nitrate by treatment with sulphuric acid, about 72 per cent of the sodium nitrate being nitric acid. As the by-products of this operation only partially pay the costs, the manufacturing costs leave the nitric acid with a value of 50 per cent over the value as nitrate. Hence a chemical works could afford to produce nitric acid when they could not afford to add a manufacturing cost to produce a fertiliser from the nitric acid, and then sell it in competition with the crude Chile nitrate.

A large portion of the phosphate rock of this country is treated with sulphuric acid to form the so-called superphosphates. If nitric acid is used in place of sulphuric acid, the superphosphate can be produced at the same time as a fertiliser of lime nitrate, or, if preferred, a high concentration of phosphoric acid can be produced from lower-grade phosphate rock. Industries of this kind promise more favourable results commercially than does the direct production of fertiliser. If low-grade products are manufactured at close prices, a very large volume of business is a necessity, and works of this character and magnitude are more apt to be a result of successful development rather than an initial venture in a field beset with uncertainties as to the profits and the chances of development of other processes reducing these if they are problematical.

Costs of making Products.—Let us consider more in detail some of the costs. We may assume approximately that the labour and repairs in furnace room and absorbing tower will cost 10 dols. per ton of nitric acid, and if nitric acid is selling for 60 dols. per ton, we have a margin for power costs, interest, general expense, &c., of 50 dols., and if we produce 500 kg. of acid per kilowatt year, it will require 2 kw.-yr. per metric ton or 25 dols. per kilowatt year, and we must absorb all interest charges and general expense in this. If the yield can be made 550 kg. per kilowatt year and we can sell for 60 dols. per short ton, we will require 1.8 kw.-yr. or 28 dols. per kw.-yr. We must assume that the product does not have to be packed for shipment and that there are no selling costs involved, and we must figure on an output so that our units may be large enough to bring the investment in plant down to 80 dols. per ton of acid, so the annual charge may be 8 dols. or net 20 dols. per kilowatt year, and if 5 dols. are allowed for general expense, the best we can do will be about 15 dols. per kilowatt year.

We see it would be hopeless to attempt to put this acid into a product to compete with the fertiliser prices, for they are some 50 per cent lower in selling price, and it will involve a cost for some raw material to mix with the acid, the cost of manufacture, and a packing and shipping charge. We must then abandon any idea of making fertiliser from nitric acid prepared by the direct oxidation of atmospheric nitrogen in the electric arc until such time as we can improve the very low efficiency due to the thermodynamic limitations of the reaction. We can only hope to utilise this process in the manufacture of nitric acid coupled with some other product which will procure for it a higher price. There is, for example, a limited demand for the nitride of sodium NaNO_2 used in the dye industry, and this is manufactured by reducing nitric acid with molten lead, thereby adding another manufacturing operation to the acid cost. This nitrite may be cheaply made by taking a mixture of NO and NO_2 , such as we would

have in parts of the system, and passing it into water or sodium hydroxide, thus, $\text{NO}_2 + \text{NO} + \text{H}_2\text{O} = 2\text{HNO}_2$, or $4\text{NO} + 2\text{NaOH} = \text{N}_2\text{O} + 2\text{NaNO}_2 + \text{H}_2\text{O}$, and this process would produce a product selling for 4 to 5 cents per pound. We must remember, however, that the price of nitric acid is not a fixture, and that a cheap combined nitrogen fertiliser will cut the price of sodium nitrate and hence the price of nitric acid. We are confronted then with the fact that all processes will be affected by the success of any one process that is a large enough success to affect the market conditions of combined nitrogen and upset the ruling prices in the fertiliser industry. It is useless to look only to cheap power as a solution of this problem, as the real solution is in the improvement of processes.

Let us roughly compare the power requirements of the processes as we have outlined them above, and we find:—

	Kw.-hr.
Direct oxidising of atmospheric nitrogen 5 per cent efficiency, yield at 550 kg. per kw.-year, requires per kg. of N	65
Cyanamide process 66 per cent efficiency in carbide 1 per cent loss in heating to combine with N, requires per kg. of N	16.6
Also preparation of N.	
Aluminium nitride using coal to heat products to temperature of reaction requires per kg. of N . .	12
Catalytic method of combining N and H to form ammonia, requires per kg. of N	1.5
Also preparation N and H, refrigeration, and compression to 200 atmospheres.	

The general tendency abroad in figuring the cost of water-power is to give only the operating costs, and from this one sees costs of producing power figured at from 50 cents to 1.00 dols. per kilowatt year, and in using these figures erroneous ideas have been widely circulated. In this country it has been standard practice to consider the investment in the power-plant; that is, the cost of the development and the property as fixing very largely the cost of producing the power. It is quite common to have labour and supplies cost not more than 1 dol. per kilowatt year, but this would not be considered as representing the cost of the power. Where a chemical industry owns the hydroelectric power-plant as well as the chemical works, the foreign practice is inclined to consider the investment as a whole and apportion the costs of operation to the various departments, while interest on the capital is charged to the profits. The costs of producing power are therefore uniformly much lower than we are accustomed to figure on. There are many plants in operation in the chemical industries abroad whose real costs of producing power are no lower than many of the more favoured locations in this country.

Off-peak Loads.—One of the chief interests in the chemical utilisation of electrical energy is centred in the possibilities of off-peak or off-season loads, as American plants generally have a certain proportion of power which can be disposed of to better advantage than selling the entire output as low-priced power to chemical industries. This off-peak power is difficult to utilise in furnace work, where the cooling of the furnace and its charge is an important factor both from the standpoint of cost and of output, and, again, adjustments may be so disturbed from an interrupted output as to be absolutely impracticable. One of the possible solutions for off-peak utilisation appears to be in the adoption of some system where fuel is also utilised and the radiation losses are not excessive under conditions of banked fire when the electric portion of the heat energy is not in use. Some of these combination processes may promise a solution of the off-peak load situation more attractive than the straight electric furnace, which is difficult to cool down entirely without unduly affecting the conditions. In all plants the volume of output is the determining factor in absorbing the general overhead charges, and any intermittance must diminish output with its accompanying disadvantages.

If the furnace could be operated on the off season load and its products stored, and the chemical works utilising this product could operate on a normal schedule, this would form one solution; or another would be, if by chance the off-season power were available at the time the greatest demands were to be met, such as preparing a fertiliser product at the season of fall rains for the early spring delivery. All of these plans, however, suggest the necessity of operating at least a portion of the plant continuously in order to meet fixed charges and preserve an operating organisation. If the chemical works require a moderate amount of power for its processes in year-around operation and only its surplus for manufacturing its crude material at the off-season peak, it promises the greatest possibilities.

The future of nitrogen fixation is alluring, and promises many developments along lines other than those we have considered, but already the market has felt the effects of these various processes, and instead of nitrogen being figured at 13 cents per pound, it is confidently predicted it will very shortly find its level at a selling price of about 8 cents, making a cost of production of 5 to 6 cents per pound, and thus reducing sodium nitrate to about 1.33 cents per pound, or approximately 30 dols. per long ton, and the lower-grade mines will feel this and be forced to curtail.

It therefore seems very certain that before twenty-five years shall have elapsed since Sir William Crookes made his memorable Address, the Chile nitrate beds will have vastly curtailed their production, not from exhaustion, but from the inroads made by the onward advance of chemical and electrochemical engineering.

NOTE ON THE CORROSION OF IRON AND STEEL.*

By S. WHYTE.

A CASE of rather rapid corrosion of a water-pipe recently came under the notice of the author. The pipe was made of the average quality of mild steel as far as chemical composition was concerned. When in use it was about three feet under the surface and in a soil of yellow clay. Corrosion had proceeded over the outside surface generally, and in places there were deep pits and in one place a perforation.

On micro-examination the steel was found to have a badly overheated structure, the ferrite having the form of straight bands with angular and elongated patches of pearlite between them. It was thought advisable to replace all the piping laid down at the same time as the bad one, but some of it when taken up showed much less corrosion, and in the latter case the only difference that was found was in the micro-structure and to the extent that the overheating had not been as bad.

While there is practically no relation between acid corrosion and atmospheric tests, the author thought an accelerated test of some sort might give some valuable information on the effect of overheating.

When studying the corrosion of copper alloys Dr. Desch and the author had found the use of an electromotive force gave satisfactory results in examining the initial stages of corrosion (*Journ. Inst. of Metals*, 1913, x., 304; 1914, xi.). Consequently the light thrown on the mechanism of corrosion in its early stages enabled the subsequent chemical and mechanical actions occurring under service conditions to be foretold with some degree of confidence.

It was thought the application of this method in the above instance might be helpful.

The experimental method is the one employed on former occasions with the improved form of apparatus to give

more accurate measurements (S. Whyte, *Ibid.*, 1915, xxxiv., 258).

The specimen to be examined is made the anode, whilst the cathode is a small square of platinum gauze. The electrolyte, which is a dilute solution of sodium chloride, is allowed to remain in contact with the metal for a definite time and is then withdrawn and analysed. The electromotive force was obtained from an accumulator, and was kept constant by means of a sliding resistance and voltmeter. Iron only was estimated in the corrosion product, and the coloration method with ammonium thiocyanate was used.

Two steels were chosen of 0.28 per cent C. and 0.55 per cent C. respectively. These were overheated at about 1100° C. and cooled slowly. Portions were cut off and refined by reheating and then cooled in the same way. Specimens of accurate dimensions were prepared from the above and corroded under identical conditions. A series of results under varying e.m.f.'s and durations of tests show that the corrosion product from the overheated specimens is on an average about 20 per cent more than that from the normalised ones.

Microscopical observations show that the free ferrite is first attacked, and on further corrosion a reversal takes place, and the pearlite becomes relatively more attacked. This was observed by Dr. Desch and the author on a former occasion (*Journ. W. of Scot. Iron and Steel Inst.*, 1914), when the reversal corresponded to a maximum in the extraction of manganese by the electrolyte. On still further corrosion the free ferrite is again attacked relatively more than the pearlite, and much more so in the overheated specimens. In a two minutes' test the ferrite of the normalised specimens was 1.5 thousands mm. below the pearlite areas, while in the overheated specimens it was 2.2 thousands mm. below.

As the difference of electric potential between adjoining crystals stimulates corrosion along the boundaries, it might be that the increase in the boundaries due to overheating is responsible for the increased amount of corrosion. Also in the reversal action, when the free ferrite is attacked in preference to the pearlite, the ferrite lamellae of the pearlite is protected by some sort of local polarisation, so that in a normalised steel, when the free ferrite and pearlite are intimately intermixed, the tendency would be to form the maximum number of these local couples, and thus give a minimum of corrosion.

Although the above method points to an increase in the amount of corrosion due to overheating, it is clear this method is only suitable for examining the initial stages, and it is possible that the subsequent mechanical actions might possibly reverse this, but the grain of the overheated steels being coarse and open the chemical products of corrosion are not likely to be so adherent as with fine-grained specimens, so that it is probable the subsequent actions are more or less on a parallel with the initial ones.

THE ZINC-COPPER-COUPLE HYPOTHESIS OF BRASS CORROSION.*

By ARNOLD PHILIP, Admiralty Chemist.

MANY investigators have attributed the corrosion of two-phase brass by sea-water to the action of small electrolytic currents set up by minute couples of adjacent crystals of metal of different phase (Milton and Larke, *Proceedings of the Institution of Civil Engineers*, 1903, cliv., 27), and it has been suggested that even grains of differently oriented crystals of a single phase may act in the same manner.

As far as the author is aware, it has not, however, yet been suggested that the corrosion of commercial brass consisting of the α , the α_1 , β , and the β phases may

* A Contribution to a General Discussion on "The Corrosion of Metals" held before the Faraday Society, December 8, 1915.

* A Contribution to a General Discussion on "The Corrosion of Metals," held before the Faraday Society, December 8, 1915.

be due to the action of minute zinc-copper couples acting as small electrical cells all over the surface of the brass. It is to this view that it is now desired to call attention. It has long appeared to the author that much might be advanced in support of this idea, and the present opportunity appears advantageous for bringing forward some of the facts which seem to lend probability to the zinc-copper-couple hypothesis.

As a preliminary it must be remarked that hitherto the author has not been successful in devising any completely convincing test which will demonstrate by itself that the corrosion of brass when immersed is an electrolytic action of zinc-copper couples on its surface, but on the other hand he has been equally unsuccessful in obtaining definite evidence that this action does not take place. Nevertheless, the explanations which this hypothesis offers of many peculiarities of brass corrosion, when considered as a whole, do give a considerable amount of circumstantial evidence in its favour.

Both the α and the β phases of brass consist of solutions of zinc in copper, and no evidence of any chemical combination between the two elements is known to exist.

The surface of such brass may therefore reasonably be considered to consist of surfaces of zinc and copper in close contact.

The corrosion of industrial brasses, whether carried out electrolytically by an external electromotive force or by any other means, has never been known to cause the separation from the brass of any other metal or inter-metallic phase except copper. It has repeatedly been shown that although under suitable conditions copper may be separated from brass under a process of dezincification, the metallic corrosion residue always consists of (a) the unaltered brass or (b) pure metallic copper or a mixture of both.

The foregoing facts may be considered to furnish an indication of the possibility, if not the probability, that brass corrosion may be due to the mutual electric action of the copper and the zinc contained in it as such in the presence of an electrolyte.

The behaviour of brass immersed in sea-water may be conveniently considered under three principal heads:—

1. *Auto-corrosion*, due to the action of sea-water upon brass immersed in it out of contact with any other electrically conducting body.

2. *Contact-corrosion*, due to the action of sea-water upon brass immersed in it when it is in contact with some other solid conductor also immersed or partially immersed in the sea-water.

As examples of such other conducting solid bodies the following may be considered:—

(a) A more electro-negative solid than copper, as, for instance, coke.

(b) Copper.

(c) A less electro-negative solid than copper, but more electro-negative than zinc, as, for instance, cuprous oxide.

(d) Zinc.

(e) A more electro-positive solid than zinc, such as, for instance, magnesium.

3. *External current corrosion*, due to the action of sea-water upon brass immersed in it when an externally generated electric current flows through the surface of contact between the brass and the sea-water. This current may pass—

(a) From the brass into the sea-water, or

(b) From the sea-water into the brass.

1. Auto Corrosion.

Taking the first case, that of the corrosion of brass immersed in sea-water without contact with any other conducting solid body. Here, if the zinc-copper couples' action is the cause of corrosion, a current flows from each zinc element, zinc chloride being formed, to each copper

element, where caustic soda is formed and a certain amount of hydrogen is deposited on the copper; if no depolarising material such as oxygen is present in the water, the action quickly ceases, due to polarisation, and we have the case of a piece of brass immersed in sea-water free from oxygen, and under these circumstances as has been repeatedly shown, no corrosion loss or dezincification occurs. If, however, sufficient oxygen is present in the water to just oxidise the hydrogen as it is deposited the current continues at its highest possible value and a maximum corrosion of the zinc occurs, whilst the copper being just protected from oxidation, marked dezincification is observed. If, on the other hand, the supply of oxygen is in excess of that necessary to oxidise the hydrogen liberated by the corroding currents, the copper becomes oxidised to suboxide of copper. This substance, however, is less electro-positive than zinc but more so than copper, and hence the current flowing from the zinc falls in strength, whilst a small amount of current flows from the cuprous oxide areas to any copper areas, forming copper chloride from the copper oxide and depositing hydrogen on the copper.

The above statement of the zinc-copper couple action will therefore cover the general case of the auto-corrosion of a piece of brass immersed in sea-water without contact with any other conducting solid. The phenomena which have been experimentally observed are:—

1. If oxygen is absent from sea-water no corrosion occurs.

2. If oxygen is present—

(a) Dezincification and separation of metallic copper may occur; or

(b) Solution of the zinc and corrosion of the copper without the separation of copper; or,

(c) A combination of 1 and 2 in which both copper oxide and metallic copper are separated, whilst the zinc is dissolved.

3. If the temperature is raised with the same proportion of oxygen in the water, corrosion is accelerated, due to the fact that the conductivity of the water is increased whilst the e.m.f. of the zinc-copper couple is also raised, thus increasing the magnitude of the corroding currents.

4. If the strength of the electrolyte is increased, as when concentrated sea-water is used at either the normal temperature or at a higher temperature, we again have the corroding currents increased, because once more both the conductivity of the solution and the c.m.f. of the couple are raised. Conversely, if a diluted sea-water is used the corrosion is diminished.

5. If the oxygen content of the water is raised corrosion increases.

6. If the water is agitated corrosion increases, because, firstly, more oxygen is introduced, whilst secondly, the polarising deposits and solutions of zinc chloride and caustic soda formed respectively at the surfaces of the zinc and of the copper are continually removed and replaced by the pure sea-water. It is observed in this connection that zinc in the zinc chloride solution formed and the copper in the caustic soda solution formed both give smaller e.m.f.'s than the same metals in the unaltered sea-water. This is also in accordance with the general law that the decompositions of an electrolyte in which any pair of electrically connected elements are immersed always lower the original e.m.f. at each element, and the same is also true of the material, if any (such as hydrogen on the copper), which is deposited by the current.

7. With dilute sea-water dezincification of brass is more marked than with the normal undiluted water (Bengough and Jones, *Journal of the Institute of Metals*, x., 40).

Passing next from the general case of the corrosion of any alloy of zinc and copper containing only the α , α and β , or β phases to the particular cases of copper-zinc alloys containing varying percentages of zinc, we find that the higher the percentage of zinc present—

(a) The lower is the rate of corrosion for sea-water

containing a given oxygen content (*Ibid.*, 1913, x., 32); and

(b) The greater tendency is there for dezincification to appear (*Ibid.*, 40 and 41).

In connection with the fact that their observation showed repeatedly that Muntz metal corroded more slowly in normal stagnant sea-water at ordinary temperatures than was the case with 70/30 brass under the same conditions, Messrs. Bengough and Jones remark: "These results are surprising. In the first place it would be expected that the Muntz metal tube would suffer the greatest loss of weight, since it is a two-phase system and would therefore appear to be peculiarly liable to electrolytic action. . . . The 70/30 brass is a homogeneous single-phase system and would be expected to show less loss of weight." The present writer would be inclined to fully agree with these investigators' conclusions if the corrosion of brass is to be considered as being due to the electric couples formed by different phases of the copper-zinc alloys. If, on the other hand, the action is considered as being due to electrolysis produced by zinc-copper couples, an opposite conclusion must, it is considered, be arrived at.

For if a mass of brass is acted upon by an electrolyte so that the metallic zinc is corroded away, the corrosion loss consists not only of the zinc dissolved away and the copper which has been chemically attacked, but also of the spongy copper remaining, if any dezincification has taken place. Hence in a 70/30 brass, if 30 parts of zinc are dissolved, 100 parts of brass are corroded and destroyed, whilst in a 60/40 brass, if 30 parts of zinc are dissolved, only 75 parts of brass have been destroyed. Thus, if a piece of 70/30 brass and a piece of 60/40 brass are both suspended in the same sea-water, but are not in contact with each other or any other conducting body, and if it is supposed that the molecular currents from the zinc-copper couples per unit area of the surface in contact with the sea-water of each of the samples is the same, it must be admitted that the weight of zinc dissolved per unit area per unit of time must be the same for both the 70/30 brass and for the 60/40 brass, and therefore, from what has been said above, the weight of the 70/30 brass destroyed per unit area per unit of time must be greater than the weight of 60/40 brass destroyed on the same area in the same time in the ratio of 100 to 75 or 1.3.

But, further than this, consideration will show that the molecular currents from the zinc-copper couples per unit area of the 60/40 brass cannot be equal to the similar molecular currents per unit area of the surface of the 70/30 brass: for each unit of area of zinc in the copper-zinc couples on the surface of 60/40 brass has a corresponding area of copper in approximately the ratio of 1 of zinc to 1.5 of copper, but in the 70/30 brass the ratio of the zinc to the copper areas is approximately 1:2.5. Hence in 60/40 brass under corrosion in sea-water, for a given amount of molecular current from the zinc-copper-couples per unit of area of brass surface a greater amount of hydrogen is deposited per unit area of copper, and hence more polarisation must occur than is the case where a 70/30 brass is corroded in the same solution.

Not only this, but as the oxygen which acts as a depolariser performs this function chiefly on the surface of the copper, if the surface of the copper is reduced the depolarisation becomes less active.

For both these reasons it is clear that the molecular corroding currents from the zinc-copper-couples per unit area of the surface of 60/40 brass when immersed in sea-water must be not equal to but less than the similar molecular currents per unit area of 70/30 brass corroded under the same conditions.

Hence the ratio of the destruction of 70/30 brass per unit area to that of 60/40 brass when both are exposed for the same time to the same electrolyte is not only in the ratio of 1.3, as has been shown would be the case if the zinc-copper-couple currents were equal per unit of surface area exposed to corrosion, but must be something greater

than this by an amount which it is difficult to calculate theoretically.

Messrs. Bengough and Jones, in the Second Report to the Corrosion Committee of the Institute of Metals, have published several results of pairs of simultaneous corrosion tests on 70/30 brass and on 60/40 brass in both normal sea-water, diluted sea-water, and concentrated sea-water at both atmospheric and also at higher temperatures. Each pair of tests was carried out under identical conditions. Calculations made from these results, which are summarised in the tabular statement appended, show that the values of the ratio of the corrosion rate of 70/30 brass to that of 60/40 brass under the various conditions of test used vary from about 1.55 to 2.19, whilst the minimum theoretical ratio is for these two alloys 1.30.

The zinc-copper-couple hypothesis not only offers an explanation of the more rapid corrosion of the copper-rich commercial brasses which has been experimentally observed, but it also indicates that it is to be expected that under similar conditions as to the amount of oxygen present in the water dezincification is more likely to be noticeable in the zinc-rich brasses than in the copper-rich brasses. For, given an equal volume of current per unit surface area when two brasses of different copper content are immersed in the same sea-water, the surface of the copper being smaller in the zinc-rich brass will be more densely coated with hydrogen, and will therefore be more fully protected against the action of the oxygen, the available amount of which for hydrogen-oxidation purposes must also be less, as it must be a function of the area of the copper exposed to its action, and this is less. It is therefore to be expected that a brass of high zinc contents will be more likely to exhibit signs of dezincification than

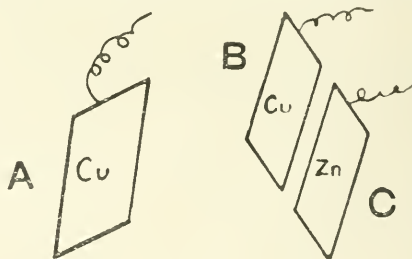


FIG. 1.

one of low zinc contents, and this, as has already been pointed out, has been observed to be the case by Messrs. Bengough and Jones.

It is of interest to attempt to make some estimate of the magnitude of the total zinc-copper-couple corroding currents which may flow per unit of surface area during the auto-corrosion of brass in sea-water. One method of making such an estimate is to calculate the total zinc lost in a given time per unit area of surface during auto-corrosion in sea-water. The most active rate of loss of weight of brass which the author has repeatedly observed in running aerated sea-water for a period of 60 days is of the order of 30 grains per square foot of surface exposed to corrosion of 100 days. If the brass is a 70/30 brass, this corresponds to a corrosion loss of 9 grains of zinc per square foot per 100 days, and this loss is equal to a current of 0.0002004 ampère per square foot of surface. Calculations made from other data given later on depending upon the corrosion of brass by an externally generated e.m.f. have shown that the magnitude of the auto-corrosion current per square foot may vary between 0.00039 ampère to 0.00346 ampère.

The mean value of the auto-corrosion currents per square foot of surface per 100 days' corrosion must of course vary with the period over which the corrosion takes place, as it is recognised that the corrosion losses are greater per unit of surface per unit of time for short than for long

Calculated Values of the Ratio of the Corrosion of 70/30 Brass to that of 61/39 Brass in Sea water, from Messrs. Bengough and Jones's Results, as given in the Second Report to the Corrosion Committee of the Institute of Metals.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Page.	Table.	Duration of corrosion in days.	Temperature of water, °C.	Condition of water.	Strength of sea-water.	Position of test pieces.	Distance of test piece below surface of water.	Loss of weight per cent of —		Ratio of loss given in Col. 9 to that given in Col. 10.
								70/30 brass.	61/39 brass.	
24	II.	208	18—20	Stagnant	Normal	Vertical	$\frac{1}{2}$ inch	0.50	0.31	1.61
24	III.	208	18—20	"	"	"	3 inches	0.45	0.27	1.66
35	IV.	120	18—20	"	"	Horizontal	1 inch	0.56	0.36	1.55
40	VI.	168	18—20	"	(a)	Vertical	$\frac{1}{2}$ inch (?)	0.57	0.30	1.90
52	VIII.	35	40	"	Normal	Horizontal	1 inch	0.24	0.11	2.19
52	VIII.	35	40	"	"	"	1 inch	0.21	0.11	1.90

(a) Equal parts of sea- and distilled water.

As the thickness of the brass upon which these tests were made was uniform, the loss of weight per cent given in Columns 9 and 10 is proportional to the loss of weight per unit area, and hence the ratio given in Column 11 is actually the observed value of the ratio of the corrosion loss per unit area per unit time for 70/30 brass to the corrosion loss per unit area per unit time for 61/39 brass. The theoretical minimum value of this ratio for 70/30 brass and 61/39 brass is 1.30.

The page and table numbers given in Columns 1 and 2 refer to vol. x. of the *Journal of the Institute of Metals*, 1913.

periods, whilst the rate of supply of oxygen and variations in temperature and rate of circulation of the water also affect the magnitude of the rate of corrosion, and hence also of the mean value of the zinc-copper-couple corroding current per unit area.

If the e.m.f. of a brass-zinc couple immersed in sea-water is measured by a zero-current method by either an electrostatic voltmeter or by a potentiometer method, it is found to be less than that of a copper-zinc couple in the same solution and at the same temperature. It might therefore be argued that the brass cannot consist of a mixture of zinc and copper elements as such, but must consist of some chemical compound of zinc and copper differing both from zinc and copper.

But this conclusion may be seen to be unwarranted if one considers two sheets of copper A and B and one sheet of zinc C, all immersed in sea-water and all insulated from each other (Fig. 1). If suitable means are taken to measure the potential difference between A and B, it is found to be zero, and between A and C it is that of a zinc-copper couple for the given electrolyte at the given temperature; but if now B and C are electrically connected, a local current flows between them and a layer of zinc chloride solution is formed over the surface of the zinc, and a layer of caustic soda solution is formed over the surface of the copper, and the difference of potential between the connected sheets of copper B and zinc C, and the sheet of copper at A is found to be less than if the copper at B were not connected to the zinc C, due not only to the fact that the electrolyte over the surface of the copper and of the zinc at B and C is no longer sea-water, but also partly to the fact that a local current is flowing between the copper B and the zinc C.

Marked and sharply localised dezincification areas in brass have repeatedly been noticed by many observers to occur beneath white crystalline deposits of what appears to be a basic chloride of zinc, which are formed upon the surface of brass when corroded in sea-water. It is a peculiarity that this type of dezincification proceeds somewhat rapidly.

If the formation of these deposits has once occurred, and if one admits that beneath them there is a somewhat strong solution of zinc chloride, it is considered that the observed rapid dezincification of the alloy can be explained on the zinc-copper-couple hypothesis, for if the strong zinc chloride solution possesses a higher conductivity than normal sea-water, and if the oxygen available is sufficiently large in amount to destroy or partly destroy the hydrogen deposited on the copper, the conditions for rapid dezincification are present.

But the full consideration of this particular form of dezincification is not yet possible, owing to the fact that

suitably devised experiments upon it have not yet been carried out. How are these crystalline deposits of basic zinc chloride first formed? Are they caused in the first instance by a preliminary dezincification which their presence then accelerates, or are the crystals first deposited on some rough surface and then initiate the acute dezincification? Do the crystals in fact initiate the dezincification, or does the denzincification initiate the crystals?

The author's opinion on this point at present is that it is a mutual action, and therefore tends to take place on a roughened surface or upon points or edges of a sample of brass. More investigation on this phenomenon is desirable, and one or two peculiarities which it presents may be remarked upon. Bengough and Jones (*loc. cit.*) have observed with regard to this action that it occurs more readily in brasses containing high zinc contents—that is, in two-phase structures—and have also found that it occurs more readily at high than at low temperatures, whilst, what is particularly remarkable, these investigators find it to occur more readily in sea-water diluted with an equal volume of distilled water than is the case if sea-water only is used.

(To be continued).

PULP FOR PAPER. AN IMPERIAL OPPORTUNITY.

THE decision of the Swedish Government to prohibit the export of wood-pulp calls attention to the enormous extent to which this country has preferred to rely on Sweden for this commodity, while all the time the resources of the British Empire, if adequately developed, are perfectly capable of supplying all our demands in this direction. Swedish wood-pulp is produced from the soft coniferous woods, such as the various kinds of fir, pine, and spruce, and in Canada and Newfoundland huge areas of these woods are still untouched, the present employment of this timber for paper-making purposes being on a scale which, compared with the natural resources of these Dominions for the purpose, is quite trivial.

Many other parts of the British Empire are, moreover, capable of supplying paper-making materials. A great variety of these materials have already been investigated at the Imperial Institute, and hardly a month passes without fresh British sources for the raw material for paper-making being brought to light.

In Central and Northern India, for instance, enormous forest areas are covered with waste grasses which are at present of little or no economic value. At least half-a-

dozen different types of these grasses yield a pulp of first-class quality. In the Mysore district the forests already explored would yield 60,000 tons of grasses per annum for paper material purposes. Large tracts of bamboos are also available in various parts of our Indian Empire for the same purpose, Lower Burma and Southern India being especially rich in this respect. Factories for working bamboos for paper have in fact already been established in the East, in Japanese Formosa, and in French Indo-China. Trials on a commercial scale have been carried out with success at a paper-mill in India, but the development of the manufacture has been hindered by the war.

British Africa offers an alternative paper making material in the "elephant grass" of Uganda, a perennial grass occurring in a wide zone across Tropical Africa, which is a source of great annoyance and expense to agriculturists in that Protectorate. A first-rate pulp was prepared from this grass at the Imperial Institute. The commercial prospects of any scheme for an industry would of course depend on the expense of manufacture and transport. The necessary chemicals and fuel for manufacture are available in East Africa. The supply of "elephant grass" is practically inexhaustible, the land on which it is grown being now regarded as "bush."

Other promising paper-making materials which have been reported on by the Imperial Institute come from the Sudan, South and East Africa, British Guiana, the Federated Malay States, and the British West Indies, where, at Trinidad, a factory is at work turning out pulp from the sugar-cane residues, hitherto used only for fuel.

NOTICES OF BOOKS.

Annuaire du Bureau des Longitudes for 1916. Paris: Gauthier-Villars. 16mo., about 700 pages, with 41 figures and 3 magnetic plates. 1 fr. 50 c.

THIS *Annuaire*, so valuable for the number of useful papers it contains, has just been published. The excellent collection contains, after the usual astronomical information, tables referring to metrology, monies of all nations, geography, statistics, and meteorology. The work is not only useful on the table of the technologist, the physicist, and the mathematician, but every one will value it as placing before his eyes the usual list of natural constants, and also for the interesting notice given this year by M. Bigourdan on "The Mean Barometric Pressure and the Occurrence of the Winds in France" (with many figures). The Supplement giving the Calendar for 1917 will also be highly appreciated by the reader.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 24, December 13, 1915.

Preparation of Phosphorescent Calcium Sulphide.—Pierre Breteau.—Verneuil has stated that to prepare phosphorescent calcium sulphide the following mixture must be heated to bright redness in a Perrot furnace:—Calcium carbonate, 100 parts; sulphur, 30 parts; sodium carbonate, 2 parts; sodium chloride, 0.12 parts; bismuth subnitrate, 0.02 parts. The author finds that the sodium salts are not indispensable, and it is best not to use a Perrot's furnace. He proceeds as follows:—Calcium sulphide is prepared by heating for an hour in a muffle furnace a mixture of 100 grms. of calcium carbonate and 30 grms. of sulphur. After cooling, 10 grms. of the calcium sulphide is made into a paste with absolute

alcohol, and 1 cc. of a solution of basic nitrate, containing 0.30 of basic nitrate in 200 cc. of absolute alcohol, is added. The paste is dried and heated to nascent red heat for two hours. The sulphide thus prepared possesses a beautiful violet phosphorescence. A phosphorescent sulphide can also be prepared by adding to the mixture of calcium sulphide and bismuth 1/100 of its weight of sodium sulphide.

Bulletin de la Société Chimique de France.

Vol. xvii.-xviii., No. 21—22, 1915.

Anomalies in the Decomposition of Aspirin by Water.—D. E. Tsakalotos and S. Horsch.—The velocity of the decomposition of aspirin by water, measured at the ordinary temperature (20°), at 50°, and at 60°, has two minimum values. This decomposition is an example of those rare reactions the velocity of which passes through minimum values. The first case was observed by Wijs in his classical studies of the saponification of methyl acetate by water. The decomposition of aspirin by water is a very complicated reaction; the anomalies are probably due to the catalytic action of the H and OH ions.

m-Phenetidine and some of its Derivatives.—Frédéric Reverdin and J. Lokietek.—The authors have prepared *m*-phenetidine as follows:—*m*-Acetylaminophenol is dissolved in an alcoholic solution of caustic potash by heating on a water-bath. Then ethyl bromide is added, and the heating is continued. The addition of water to the filtered solution precipitates acetyl-*m*-phenetidine, which may be saponified by heating on the water-bath with hydrochloric acid and then treating with caustic soda and separating the free base by decantation. The base is a colourless liquid boiling at 248°; it turns brown when exposed to the air and light. The authors have prepared many of the acyl derivatives by the usual methods and have investigated their properties. They have also obtained some azoic colouring derivatives.

MISCELLANEOUS.

The Royal Society.—At the meeting on December 9, 1915 (Sir J. J. Thomson, O.M., President, in the Chair), the Croonian Lecture for 1915 was delivered by Dr. W. M. Fletcher, F.R.S., and Prof. F. G. Hopkins, F.R.S., on "The Respiratory Process in Muscle, and the Nature of Muscular Motion."

Liebig's Extract of Meat Co., Ltd.—The Directors of this Company have resolved to declare an interim dividend of 10 per cent free of Income Tax on the Ordinary Shares of this Company, being 10s. per share, payable on and after February 22 next to the Proprietors of the Ordinary shares registered on the Company's books on February 12, and to holders of Ordinary Shares to Bearer.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Royal Society of Arts, 4.30. (Fothergill Lecture). "National and Historic Buildings in the War Zone—their Beauty and their Ruin," by the Rev. George Herbert West, D.D.

TUESDAY, 8th.—Royal Institution, 3. "Nerve Tone and Posture," by Prof. C. S. Sherrington.

WEDNESDAY, 9th.—Royal Society of Arts, 4.30. "The Organisation of Scientific Research," by Prof. J. A. Fleming.

THURSDAY, 10th.—Royal Institution, 3. "Measurement of the Brightness of Stars—Visual and Photographic Magnitudes," by Sir Frank Watson Dyson.

—Royal Society. "The Theory of the Helmholtz Resonator," by Lord Rayleigh. "Oxyhydrogen Flame Spectrum of Iron," by Sir N. Lockyer and H. E. Goodson. "Consumption of Carbon in the Electric Arc—II, The Anode Loss," by W. G. Duffield and M. D. Waller. "Surface Friction—Experiments with Steam and Water in Pipes," by C. H. Lander. "Structure of Broadened Spectrum Lines," by T. R. Merton.

FRIDAY, 11th.—Royal Institution, 5.30. "Egyptian Jewellery," by Prof. W. M. Flinders Petrie.

SATURDAY, 12th.—Royal Institution, 3. "The Shakespeare Tercentenary—Shakespeare as National Hero," by Sir Sidney Lee.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2933.

THE HODGES PNEUMATIC TROUGH.

IN place of ordinary troughs, which are more or less cumbersome, Rev. Rattenbury Hodges has devised a very simple contrivance, or rather two types of one.

An oak tub of 18 inches internal diameter and 8 inches deep, is provided with five small wooden supports around and within it, at equal distances and 4 inches below the water-level. These are screwed on from the outside. Each support ($2\frac{1}{2}$ or 3 in. $\times$ 1 $\times$ 1 in.) is provided with a semi-circular hollow, in which a marble is made to roll freely.

A circular shelf (loosely fitting the tub) rests on these supports. It is about an inch thick, and has a round hole in its centre ($2\frac{1}{2}$ or 3 in. diameter), and is also pierced by five or six holes ($\frac{3}{4}$ or $\frac{1}{2}$ in.), at equal distances within the circle. A small knob fixed at some point near its periphery serves to turn the shelf without wetting one's fingers.

Beneath the shelf, each small hole is provided with a zinc funnel; a broad collar of sheet lead surrounds the

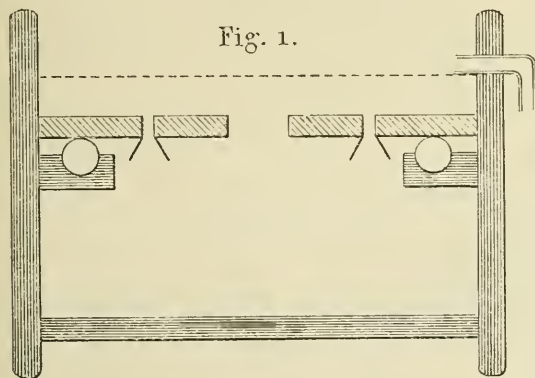


Fig. 1.

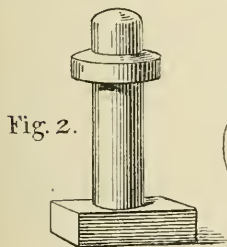


Fig. 2.

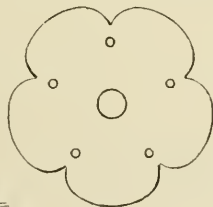


Fig. 3.

(Not to Scale).

central hole, also on the underside. Within 2 inches or so of the top of the tub, a short rectangular overflow pipe is fixed, preferably of brass, and half an inch or more in diameter (Fig. 1).

The inside of the tub is coated with good enamel paint, and the supports soaked in hot paraffin wax previous to fixing. The overflow pipe is, of course, connected by rubber tubing, with a receptacle below the bench.

With this apparatus ready for use, it is obvious that the delivery tube is put into the central hole, and the jars are charged in succession by rotating the shelf.

In the second type of trough, the circular shelf is made to revolve upon a short fixed (or screwed) post (Fig. 2).

This shelf, weighted beneath like the other, is shaped and perforated as shown in Fig. 3.

The post should not project more than 2 inches above the shelf.

THE ZINC-COPPER-COUPLE HYPOTHESIS OF BRASS CORROSION.*

By ARNOLD PHILIP, Admiralty Chemist.

(Concluded from p. 59).

1. Auto Corrosion (continued).

THE same investigators have also observed that zinc chloride crystals when placed in contact with a brass tube at ordinary temperatures did not produce dezincification, but that when heated to 70–80° C. marked dezincification appeared.

As far as the author is able to follow Messrs. Bengough and Jones's work on the dezincification of brass, he gathers that they have never observed dezincification without at the same time observing an overlying white crystalline deposit of basic zinc chloride. The author, on the other hand, believes that he has observed dezincification without any appearance of zinc chloride crystals; but this may be due to the fact that the crystals were there, but were of so microscopic dimensions that their presence was overlooked. The relationship between dezincification and these crystals deserves further investigation.

In so far as what the author terms the auto-corrosion of brass is concerned, the zinc-copper-couple hypothesis appears to be in contradiction of the fact observed by Chief Engineer Isherwood, of the United States Navy, that the corrosion per unit surface area of thick brass is less than the corrosion per unit area of thin brass exposed to sea-water under the same conditions of time, temperature, oxygenation, &c. (G. D. Bengough, Report to the Corrosion Committee of the Institute of Metals, 1911). It must, however, be stated that it is not known that Isherwood's experiments on this point have been confirmed or contradicted by results obtained by any other observer.

The zinc-copper-couple hypothesis of corrosion also does not appear to offer any explanation of the fact observed by O. Sackur that brass alloys of high copper contents will not deposit metallic copper from solutions of certain copper salts, although brasses of lower copper contents will deposit copper from the same solutions.

Experiments on the behaviour of brass in solutions of both copper and zinc salts are now being carried out by the author in order to ascertain as to whether this aspect of the question will give any useful indication as to an experiment which will finally settle this matter in one sense or another.

It has often been noticed in the course of experiments on the corrosion of brass in sea-water that a rough surface tends to cause more marked corrosion, and it is considered that the peculiarity is sufficiently accounted for on the zinc-copper-couple hypothesis of brass corrosion if it is considered that due to roughness of the copper surface the polarisation of the copper is decreased for a given oxygen supply in the electrolyte because the hydrogen deposited from the current and oxygen deposited from the sea-water both tend to collect at rough points; i.e., points of maximum curvature, and hence the two gases, the polariser and depolariser, are brought into contact with each other, and the resultant destruction of the hydrogen prevents the decrease of the corroding current which would otherwise occur on a smooth surface.

2. The Contact-corrosion of Brass.

If, as shown diagrammatically in Fig. 2, two pieces of copper sheet, Cu₁ and Cu₂, and one piece of zinc sheet, Zn₁, are immersed in electrolyte and are connected by the

* A Contribution to a General Discussion on "The Corrosion of Metals," held before the Faraday Society, December 8, 1915.

wires, a , b , and d , which are all out of contact with the electrolyte, whilst the three galvanometers A , B , and D are placed in circuit with each of the wires, and if there is an open contact key at P , then before this contact is closed it will be observed that the currents passing through a and b as read by the galvanometers A and B are equal. If now the key at P is closed, the current passing through the wire as read on the galvanometer A is found to have increased, whilst the current passing through the wire b as read on the galvanometer B is found to decrease, and a current now flows through the wire d as shown on the galvanometer D , and this current is the difference between the currents in A and B which flow after the key at P is closed.

This simple experiment illustrates the action of the contact-corrosion of brass when the brass is electrically connected with a mass of copper, Cu_2 .

The current through the zinc, Zn_1 , in the brass has been increased from the value it had before being connected to the copper, Cu_2 , and hence its corrosion is increased proportionately. That is, the auto-corrosion current has

where e is the zinc-copper-couple e.m.f. in the particular electrolyte.

This current then represents the auto-corrosion current from a unit zinc-copper couple and corrodes the zinc. The expression for this current depends only on the nature of the electrolyte as represented by the e.m.f. e and by the resistance g of the path of the current through this electrolyte, and on the thickness and nature of the brass plate that is on the resistance of the path of the current through it which is represented by the symbols a and b .

After the larger mass of copper, Cu_2 , has been placed in contact with the brass by closing the key at P , the current from the zinc rises to—

$$A_1 = \frac{e}{a + \frac{(d+f)(b+g)}{b+g+d+f}}$$

Or, as b and g are constants it is simpler to write $(b+g)=K$, when the auto-corroding current from the zinc becomes—

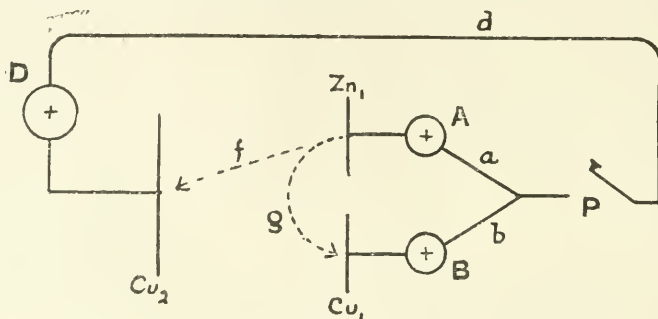


FIG. 2.

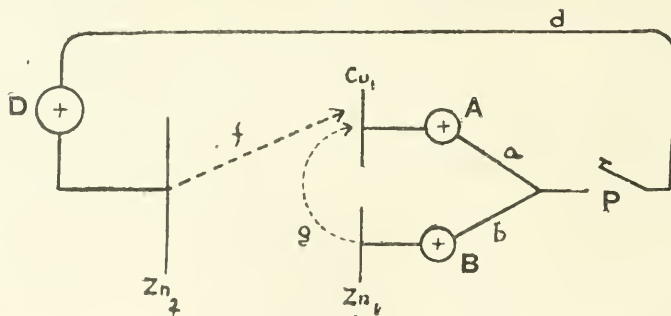


FIG. 3.

been increased to a contact-corrosion current which has a greater magnitude.

If in Fig. 2 the resistances of the connecting wires and of the circuits through the electrolyte are denoted by the letters a , b , d , f , and g , as shown, and if the resistance of the galvanometers is imagined to be zero, the resistances a and b will represent the resistances of the contact of a contiguous pair of zinc, Zn_1 , and copper, Cu_1 , particles on the surface of a piece of brass exposed to corrosion in contact with a mass of copper, Cu_2 , both immersed in any electrolyte. Whilst the resistance d is the resistance of the contact between the brass and the mass of copper, Cu_2 , and finally f is the resistance through the electrolyte between the copper mass, Cu_2 , and the brass, and g is the resistance through the electrolyte between the particle of copper, Cu_1 , and the contiguous particle of zinc, Zn_1 , on the surface of the brass. A simple calculation shows that the current flowing between the contiguous particles of zinc, Zn_1 , and copper, Cu_1 , before closing the key at P is—

$$\frac{e}{a+b+g} = A,$$

$$\frac{e}{a+k} = A_1,$$

whilst the corroding current from the zinc, when put into contact with the copper mass, Cu_2 , i.e., when the brass is put into contact with the copper, becomes—

$$\frac{e}{a + \frac{(d+f)K}{K+d+f}} = A_1,$$

and the increase of the zinc corroding current is—

$$\begin{aligned} &= A_1 - A = \frac{e}{a + \frac{(d+f)K}{K+d+f}} - \frac{e}{a+K} = \\ &= \frac{eK^2}{a^2K + aK^2 + (d+f)(a+K)^2} \end{aligned}$$

All the quantities involved in this expression for the increase of the zinc auto-corroding current caused by its contact with the mass of copper, Cu_2 , are constants except d and f . These are respectively the resistances of the

metallic connection between the copper, Cu_2 , and the brass, and the resistance of the path through the electrolyte between the copper, Cu_2 , and the brass, and it is evident that the smaller either or both of these quantities are the greater will be the current A_1 , and therefore the corrosion of the zinc caused by the contact between the brass and the copper, Cu . The limiting maximum value of this current when $d=f=0$ is therefore $\frac{e}{a}$.

In order to secure the maximum corrosion due to copper in contact with brass it is therefore necessary that the contact between the brass and the copper should have as low a resistance as possible, and the area of the copper exposed to the sea-water should be as large as possible, and the distance between the copper and the brass through the electrolyte should be as small as possible.

In precisely the same manner the decrease in current through the zinc of the brass, and therefore of corrosion of the brass which is caused by connecting the brass to a mass of zinc in the sea-water, may be observed experimentally if the circuits are arranged as shown in Fig. 3.

Before closing the key at P the currents A and B in the resistances a and b are equal, but on closing the key at P the current in a increases from A to A_1 , and the current in b decreases from B to B_1 ; that is, the corrosion of the zinc decreases from its auto-corrosion value—

$$\frac{e}{a+b+g} = B$$

to a smaller value—

$$e \left\{ \frac{d+f}{a(d+f+b+g) + (d+f)(b+g)} \right\} = B_1;$$

but, as before, b and g are constants, and if $(b+g)=K$, the zinc current through b , after closing the key at P , falls to—

$$B_1 = e \left\{ \frac{d+f}{a(d+f+K) + (d+f)K} \right\};$$

and the amount of decrease is—

$$B - B_1 = \frac{aK}{(a+K)^2(d+f) + aK(a+K)};$$

and as all the quantities in this expression are constants except d and f , it is evident that the smaller either d or f or both are made the greater will be the reduction of zinc auto-corrosion in the brass caused by connecting the brass to a mass of zinc. In the best conceivable case for a zinc mass electrolytically protecting brass from corrosion, d and f could in the limit both be zero, and then the fall in the zinc auto-corroding current would also be to zero; that is to say, the brass would be completely protected from corrosion; but as a matter of fact neither d nor f can be reduced to zero, and in most cases f must be moderately large, therefore the auto-corrosion current theoretically can never fall to zero, and the contact of a mass of zinc with brass in an electrolyte cannot completely protect it from corrosion. But in all the foregoing remarks no consideration has been paid to the fact that an alteration of the polarisation of the copper may occur by the deposition of hydrogen on the copper in larger or smaller amounts than when the mere auto-corrosion is taking place.

This alteration of polarisation does, as a matter of fact, occur. The increased current to the copper in the brass when the brass is in contact with a mass of zinc covers the copper areas in the brass more completely for the same conditions of electrolyte and temperature, &c., than when auto-corrosion only is taking place; hence the zinc corrosion currents not only fall by the amount shown above, but they decrease by a greater amount, and may reduce the zinc corrosion currents practically to zero, in spite of the fact that d and f have some reasonably high values.

The effect of the contact of solid conducting bodies which possess either a higher negative contact e.m.f. with sea-water than is the case with copper, as, for instance,

coke, or a higher positive contact e.m.f. with sea-water than is the case with zinc, as, for instance, magnesium, or, finally, with such a body as cuprous oxide, which possesses a contact e.m.f. with sea-water which is intermediate between the values given by zinc and copper under the same conditions—the effect of such contacts is similar in its nature to that caused by the contacts with zinc and copper respectively as considered above, except that the increase of the zinc corrosion currents is more marked with coke than with copper, and, moreover, direct electrolytic solution of the copper takes place, whilst with magnesium (which has, not however, been experimented with) no doubt the protective layer of hydrogen formed by zinc protectors on the copper of the brass is extended to the surface of the zinc.

3. The External Current Corrosion of Brass.

The simplest case to consider is that in which the current flows from some suitable anode in the electrolyte to the brass; here it deposits both caustic soda and hydrogen, and effectively protects the brass from further corrosion.

This is the process used commercially under the Cumberland method for protection from corrosion. Useful and interesting as this method of combating corrosion is believed to be, it has, as far as the author is aware, little or no light to throw upon the validity or otherwise of the copper-zinc-couple hypothesis of corrosion of brass, and therefore no further remarks need be made concerning this case of the effect of currents on brass corrosion.

The second case, in which an externally generated current passes from brass into an electrolyte, is, however, of a good deal of importance, and has been studied by Milton and Larke (*Proc. Inst. Civil Eng.*, 1903, cliv., 4), and in more detail and more recently by Desch and Whyte, "The Microchemistry of Corrosion," Part I., *Journ. Inst. of Metals*, No. 2, 1913, x., 304; Part II., Whyte and Desch, No. 1, 1914, xi., 235; Part III., Whyte, No. 1, 1915, xiii., 80.

This aspect of brass corrosion is of much interest as bearing upon the zinc-copper-couple hypothesis. For if an electric current flows from a brass surface supposed to consist of contiguous areas of zinc and copper, and if the current density is sufficiently high, it must be regarded as flowing not only from the zinc areas, but also from the copper areas, and as under these circumstances no hydrogen is liberated at these surfaces, no question of polarisation can occur due to hydrogen on either the zinc or the copper. Further, as each area of zinc and each area of copper possesses a distinct contact e.m.f. with the electrolyte, and as this e.m.f. is greater with the zinc than with the copper, it is to be anticipated that the current density of the current leaving the zinc will be greater than that leaving the copper, and therefore that for equal areas of copper and zinc the rate of solution of the zinc will be greater than that of the copper, and that therefore dezincification will occur and copper will be separated in the metallic form.

If now the behaviour of a copper-zinc alloy, such as Muntz metal, containing both the α and β phases is considered, it must be concluded that the electrolysis of the metal must be concentrated on the phase richer in zinc; that is, on the β phase.

These conclusions therefore show (1) that the α phase is more slowly attacked than the β phase (which is the reverse of what occurs in auto-corrosion), and (2) that in both cases when attack takes place dezincification also occurs, whilst (3) when a brass containing both the α and the β phases is corroded the β phase is first attacked.

But these are precisely the actions which Desch and Whyte's experiments show take place.

The above remarks as to the theoretical method by which the electrolytic corrosion of brass should take place, as based upon the zinc-copper-couple hypothesis, apply of course only to the initial action, for as copper is set free the fraction of the corroding current borne by the zinc must decrease for any given phase, and the ratio of the

copper to the zinc appearing in the solution as corrosion products must increase as the duration of the corrosion increases.

And this is exactly what Messrs. Desch and Whyte's results show to be the case. In their first paper on this subject (*Journ. Inst. of Metals*, No. 2, 1913, x., 313, Table V.) they give a series of results of the corrosion of a sample of β phase brass having the composition 52.92 per cent copper and 47.05 per cent zinc.

In this series of tests the same anode of brass was corroded successively for six periods of five minutes each, and in each period a fresh quantity of 5 cc. of a 5 per cent solution of sodium chloride was used as the electrolyte. The anode was not cleaned in any way between the tests. The ratios of the copper dissolved to the zinc dissolved in each of these successive periods were as follows:—

	Ratio of copper dissolved to zinc dissolved.
First period	0.02457
Second period	0.02457
Third period	0.05320
Fourth period	0.07092
Fifth period	0.1176
Sixth period	0.1852

Messrs. Desch and White also found that cored structures in the α phase were most markedly corroded on the zinc-rich portions.

In their second paper on this subject Messrs. Desch and Whyte state (*Journ. Inst. of Metals*, No. 1, 1914, xi., 245) that the experiments which they have made confirm them in their opinion that there is no essential difference between the process of electrically stimulated corrosion (*i.e.*, what the present writer terms external current corrosion) and natural corrosion (*i.e.*, auto-corrosion), and that consequently the method of electrical corrosion they have described may be employed for the purpose of determining the probable order of resistance of alloys to corrosion. The present writer does not, however, fully agree with this view, although he considers that it is more nearly correct if referred to a comparison between the effects to be expected from what he has termed the contact-corrosion of brass with coke and external current corrosion.

The very detailed results of the external current corrosion experiments given by Desch and Whyte in the three papers they have published state in every case the total weights of both zinc and copper which either passed into solution or were altered from the metallic to the oxidised or combined form, and it has therefore been possible to calculate the actual currents which must have passed from the brass into the electrolyte from both the copper and the zinc areas of the surface of the brass (that is, assuming the copper-zinc-couple hypothesis to be correct), and as the areas of the anodes are given and the compositions of the brasses and the density of both copper and zinc are known, it has also been possible to calculate the current density in the zinc areas and the current density in the copper areas and the mean current density in the whole anode used. Further, from these results the values of the auto-corrosion currents in amperes per square foot of anode surface have been calculated, and for 70/30 brass have been found to vary from 0.000346 to 0.003174, as stated earlier in this paper. These results are of the same order as the value for the auto-corrosion current per square foot of 70/30 brass which were calculated from other auto-corrosion data, namely, 0.0002004, but the values as calculated from Desch and Whyte's results, in which the exposure to corrosion in sodium chloride solution occupied only sixty minutes at the longest, are markedly higher than in those calculated from the sixty-day auto-corrosion of 70/30 brass in sea-water. As, however, the mean rate of auto-corrosion of a brass decreases markedly with the length of the period of corrosion, it is to be expected that the mean auto-corrosion current per square foot, when obtained from auto-corrosion lasting

for a period of sixty days, should be lower than the mean auto-corrosion current per square foot of anode calculated from corrosion lasting usually only five minutes, and at the most never more than sixty minutes, as was the case in Desch and Whyte's experiments.

The permissible limits of time and space do not allow of a more complete development of the facts at present known which bear upon the corrosion of brass as regarded as being due to metallic couples, but it is submitted that the facts here put forward do prove that undoubtedly such corrosion can only be explained by the action of metallic couples. This view does not, however, necessitate the further conclusion that these metallic couples are copper-zinc couples, but as this latter hypothesis explains several facts, which the assumption that couples are formed of different phases of the copper-zinc alloys does not do, and as zinc and copper are not in a state of chemical combination in either the α or the β phase, it is considered that much probability at present attaches to the zinc-copper-couple hypothesis of brass corrosion.

DEMONSTRATION OF THE CUMBERLAND ELECTROLYTIC PROCESS FOR PREVENTING CORROSION OF ALL METALS IMMERSSED IN LIQUIDS.*

By ELLIOTT CUMBERLAND.

WHILE some investigators have been studying the question of producing a non-corrodible metal others have given their attention to the question of the protection of metals. The amount of work done in the latter direction of late years is considerable.

The Committee appointed by the Institute of Metals in the early part of 1910 to investigate the causes of corrosion of non-ferrous metals and alloys has brought forward a large amount of valuable data and information on this subject.

A notable feature is the large amount of experimental work which is being carried out by the members of this Committee. A careful study of the mode of action of certain waters is being made, and they strongly advise more attention to be given to the subject of electrochemical protection.

Mr. Samuel Whyte, in his paper dealing with the microchemistry of corrosion (Part 3, "The A, B Alloys of Copper and Zinc"), gives some very conclusive proofs that the nature of corrosion of these alloys is in all cases primarily dezincification, and points out that when in his experiments corrosion was hastened by an applied electromotive force, the nature of the action was *similar* to that found in actual service conditions.

Sometimes we have conflicting evidence, but in these cases must take the evidence which comes from actual working conditions in preference to the experimental facts brought to light in the laboratory.

Mr. G. D. Bengough and Mr. Arnold Philip differed considerably over the question of the effect of carbonaceous matter in contact with the water side of condenser tubes, and I think Mr. Philip's views meet with the approval of the majority. Practical experience has shown that such an electro-negative substance as carbon in contact with brass condenser tubes very often causes and accelerates corrosion.

Prof. Ernst Cohen, of Amsterdam, in his paper on "The Corrosion of Condenser Tubes and Sea-water Conductors," read before the Institute of Naval Architects, 1902, makes some very interesting remarks on the use of iron and zinc for protecting condenser tubes from corrosion. He says:—"If the zinc is in good metallic contact with the tubes they will not corrode, but if the

* A Contribution to a General Discussion on "The Corrosion of Metals" held before the Faraday Society, December 8, 1915.

resistance between the two metals becomes too great the protective action disappears. This seems to point to the fact that the intensity of the electric current in the system is playing a part. By increasing the intensity of the electric current by means of an auxiliary battery the protective action of the zinc is re-established." And in another part of his paper he points out that "direct electric current produced by leakages, though only very small, may give rise to corrosion." "This phenomenon will only be produced by this cause when the condenser tube is connected to the positive pole of the dynamo."

It is recognised that galvanic action is the general cause of corrosion, and the use of electro-positive auxiliary plates dates back to the days of Sir Humphry Davy. This

will later give an ocular demonstration of the futility of resorting to this kind of protection, which should be of special interest in view of the present remarkably high price of pure zinc.

The Cumberland electrolytic method consists of introducing a higher counter electromotive force to that causing the corrosive action, and has achieved success in practical working conditions for many years, and has proved itself to be the only effective method of overcoming the dezincification of condenser tubes.

This system, whereby an adequate supply of protective electromotive force can be introduced to permanently overcome all corrosive action, consists of continuous current supplied by an electroplating type of dynamo,

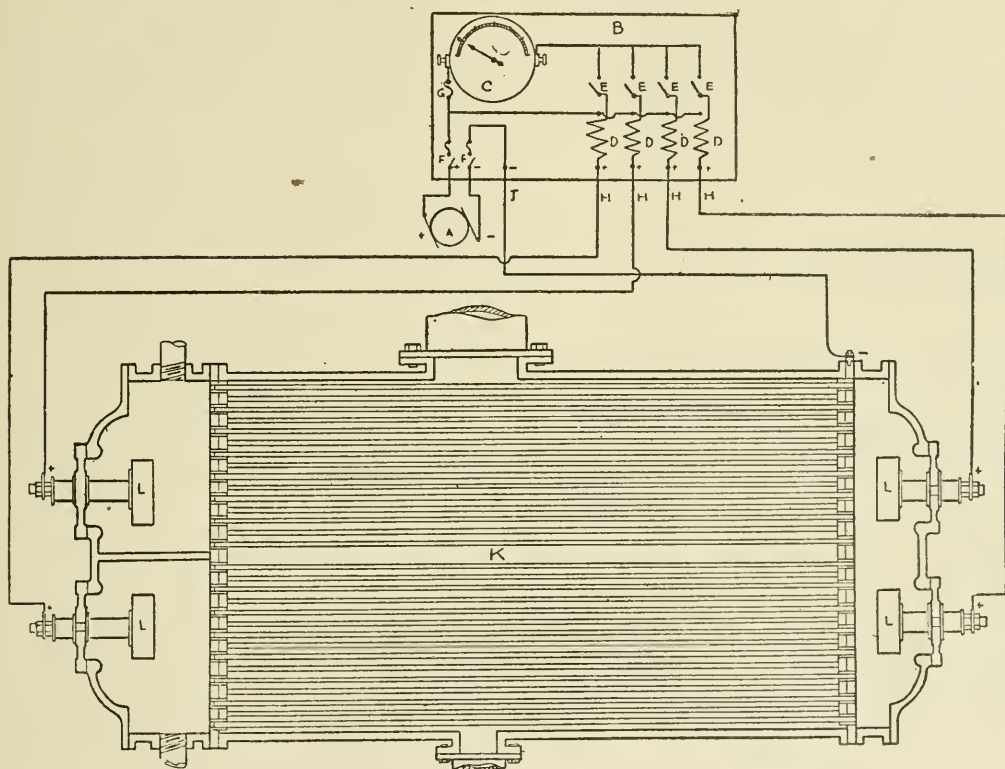


FIG. 1.—CUMBERLAND INSTALLATION ON SURFACE CONDENSER.

A, Motor Generator; B, Switchboard; C, Ampmeter; D, Adjustable Resistance Coils; E, Two-way Switches; FG, Fuses; H, Wires from Positive Pole to Electrodes; J, Wire from Condenser Shell to Negative Pole; K, Condenser; L, Insulated Bolts and Electrodes.

method is still much respected by engineers and has become sanctified by long use.

If used in sufficient quantity and properly fitted, zinc and iron are effective in lessening corrosive action of structures composed of metals lower in the galvanic or electro-potential scale. H. de B. Parsons gives the amount of zinc necessary for the protection of the internal surfaces of steam boilers as 1 sq. ft. of zinc to 50 sq. ft. of heating surface. The electro-negative metal is always protected at the expense of the electro-positive; the latter changes its formation, due to electrochemical action, and these auxiliary plates, if not frequently changed, become electro-negative to the structure and accelerate instead of retard corrosion. The rule in the British Navy is, I believe, to renew the zincs when the decomposition has gone a quarter of an inch deep in the plates.

The scale from old zinc plates can be tested and found to be electro-negative to many metals which new zinc is capable of protecting. By means of a small tank, a milliamperemeter, and a few plates of different metals I

working at 10 volts, and pieces of iron suspended in the liquid and suitably insulated from the vessel being protected. All agents to corrosion are transferred from the structure to the inserted iron, which is connected to the positive terminal, and therefore anode, and any detrimental differences of potential are overcome.

The structure is protected at the expense of these iron anodes, which are designed to last from eighteen months to two years. The attention required is that usually given to a small electric motor, and the cost of current very small, owing to the low voltage used.

For many years this system has been used in all types of steamships and many large power plants on shore, and has proved successful in severe cases when other methods had failed.

I discovered that the regular working of my electrolytic system had a most remarkable effect in removing hard scale from heating surfaces, &c., and preventing its further formation. From the steam-user's point of view this is an asset of no small importance, in view of the heat insulating

properties of scale. It has been stated on good authority that one-tenth of an inch of scale in steam boilers has been known to cause a loss in fuel efficiency of 10 per cent.

The advantages of this simple and inexpensive method of preventing corrosion and eliminating trouble from scale formation are obvious. The tank experiments will show clearly the effect of immersing dissimilar metals in water, and the zinc method of protection, also the reversal of polarity which ensues if zinc is not frequently renewed,

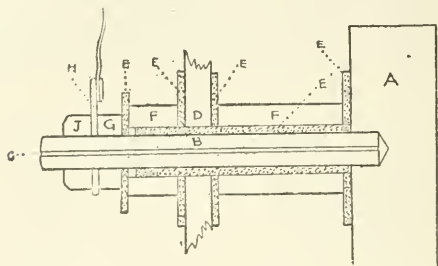


FIG. 2.

A, Electrode; B, Insulated Support; C, Tell-tale Bore; D, Condenser Shell; E, Insulation; F, Washer; G, Lug connection to Wire from Positive Pole; H, Nut.

and how by introducing a continuous current from an external source all metals can be rendered immune from corrosion.

The diagram shows my system fitted to a surface condenser. The insulated iron electrodes, L, are in all cases attached to the positive pole of the generator, and the body of the condenser is connected direct to the negative pole. All parts of the condenser in contact with the circulating water are protected at the expense of the electrodes, which are easily renewable. The amount of protective current is controlled by the adjustable resistance coils, D.

In conclusion I would point out that the use of this system is not confined to condensers alone. It may be applied with equal advantages to all types of steam boilers, economisers, feed-water heaters, tanks, propellers, and stern frames of ships—in fact all metals immersed in or in contact with water or other corrosive liquids.

APPLIED CHEMISTRY.*

By L. H. BAEKELAND.

It is only three years ago that a Brooklyn alderman, who, in the absence of the Mayor of New York, had to welcome the visitors to the International Congress of Chemistry, addressed them as if they were druggists or pharmacists.

After all, he made not much greater a mistake than many so-called educated men who obtained a B.A. and yet are ignorant enough of elementary scientific knowledge to imagine that the main occupation of a chemist is to analyse substances and detect falsifications.

Even in England a pharmacist is currently designated as "chemist," while a real chemist is called an "analytical chemist."

But the European war has done much to correct some

of these mistaken notions of the public at large. Our daily Press has to a certain extent acquainted this country with the fact that in our national make-up there are such things as chemical problems. I doubt, however, whether the unthinking masses have begun to realise that aside of the so-called chemical industry, practically every other industry, in fact every enterprise, has chemical questions to contend with, and that chemical industry itself is intimately interwoven with the great network of every modern industrial or agricultural condition; that the economic welfare of our country and the health of its citizens is largely dependent on the way we utilise our chemical knowledge.

Chemical Wars.

The present war has been aptly called a "chemical war," because efficient work of every department of the fighting armies, from the Red Cross service to the manufacture of guns and explosives, involves incessantly chemical knowledge and—still more chemical knowledge.

But do not imagine that this is the first chemical war. The art of killing and robbing each other became "chemical" the day gunpowder was invented; at that time, however, the existing knowledge of chemistry was just of pinhead size. Napoleon knew very well how to use adroitly exact knowledge and chemistry for furthering his insatiable ambition to dominate the world; so he surrounded himself with the most able chemical advisers and scientists, and, for awhile, at least, he placed himself at a decided advantage over his many enemies; incidentally, he thus helped to lay the foundation for some very important branches of chemical industry.

"Les chiens ont appris quelque chose," exclaimed the Corsican conqueror when he realised that his enemies began to adopt the same means which had given him temporary mastership over them; but those whom he called so contemptuously "the dogs" finally beat him at his own game.

Ever since then, science, technology, and chemistry in particular, have played a role of increasing importance in the armament of nations. This accounts, perhaps, for the strange fact that the really great military inventions have practically all emanated from civilians and from non-military nations like our own. If the men of the military class, essentially conservative in all countries, had been left to their own devices, they would probably still be fighting with bows and arrows—or perhaps, with the traditional sling. Nor should the pacifist blame the chemist if the latter's most beautiful conquests in science, if his proudest discoveries, have been turned into means of relentless destruction and human slaughter. Do not reproach chemistry with the fact that nitrocellulose, of which the first application was to heal wounds and to advance the art of photography, was stolen away from these ultra-pacific purposes for making smokeless powder and for loading torpedoes. Do not curse the chemist when phenol, which revolutionised surgery, turned from a blessing to humanity into a fearful explosive, after it had been discovered that nitration changes it into picric acid.

As well might you curse written speech or language or the art of printing—by which the most noble thoughts of the human race have been expressed, disseminated, and preserved—if it has been used also to distribute the vilest lies and the most damnable errors.

Knowledge is like a knife: in the hands of a well-balanced adult, it is an instrument for good of inestimable value; but in the hands of a child, an idiot, a criminal, a drunkard, or an insane man, it may cause havoc, misery, suffering, and crime.

Science and religion have this in common, that their noble aims, their power for good, have often, with wrong men, deteriorated into a boomerang to the human race. Our very successes will threaten to devour us as long as all

* Presented at the fifty-first Meeting of the American Chemical Society, Seattle, August 31 to September 3, 1915. From the *Chemical Engineer*, 1915, vol. xxii., No. 6.

of us have not yet become imbued with the truth that greater knowledge, like greater possession of wealth or power, demands a greater feeling of responsibility, greater virtues, higher aims, better men.

Let us hope, in the meantime, that war carried to its modern logical gruesomeness, shorn of all its false glamour, deceptive picturesqueness, and rhetorical bombast, exposed in all the nakedness of its nasty horrors, may hurry along the day when we shall be compelled to accept means for avoiding its repetition.

Will you take it amiss if I made a digression from my subject as an answer to some repeated attacks which have been made of late by men who blame our increasing scientific knowledge in general and our chemical science in particular, for the excesses of the present European war?

The Peaceful Work of American Chemists.

But let us turn our attention to more peaceful chemical pursuits and more particularly to the chemists of this country.

Their work is difficult to understand and still more difficult to be appreciated by the uneducated or uninitiated; nor do chemists court the plaudits of an ignorant public that cannot understand them; they feel fully compensated by the results of their work if it only meets with the approval of a few of their fellow-chemists, irrespective whether it brings them financial results or not; in fact, most chemists are so much in love with their work, that very often they neglect the financial side to their own immediate detriment.

Unlike the physician, lawyer, clergyman, actor, writer, artist, or business man, the chemist does not depend on the public at large; he is either engaged in some private enterprise or he acts in a consulting capacity for a few people, if he is not engaged as professor or teacher in some educational institution. Popularity in the usual sense has little or no value for the chemist.

No wonder then that the chemists of this country, numerous and active as they are, have hardly been noticed among the daily noise of newspaper sensation and shrieking publicity—no more than a skilful watchmaker would be noticed among the hammering of a busy steam-boiler manufacturing plant.

And yet, right here in the United States, the chemical profession has taken such a root, such a development during the later years, that we have here assembled at this very meeting, the representatives of our national American Chemical Society, which counts over 7000 members, by far the largest membership of any chemical society in the world, with all due respect to England, France, and Germany—a society which finds it possible to spend yearly over 100,000 dols. on its three chemical publications, copies of which are to be found all over the world in every well-equipped scientific library. Nor is the study of chemistry in this country a matter of recent occurrence. Our European friends are astonished when we tell them that as far back as 1792, there existed already the Chemical Society of Philadelphia, which was probably the first chemical society ever organised in the world; even to-day, some of the papers read at the meetings of that early scientific body furnish very interesting reading. Some of our American universities equipped chemical research laboratories for students, at a time when exceedingly few of the best known European universities possessed any such facilities.

Nor should we overlook the fact that notwithstanding the essentially pragmatic tendencies of our country, the United States has given to the world a Willard Gibbs, who outtheorised existing chemical theories and whose mathematical deductions are still, after his death, furnishing food for profound thought to the most renowned physical chemists of Europe, to whom they have opened entirely new fields in the study of chemical dynamics.

The Aniline-dye Situation.

I mention this more particularly because some of our aniline dye consumers have taken the chemists of the United States bitterly to task and have made decidedly unfavourable comments on their abilities, because since the European war, dyes could no longer be imported from Europe. But Dr. B. C. Hesse, an American-born chemist, a graduate of the University of Michigan, has already answered this indictment of the American chemists. In a paper full of information on this subject, which he presented at our last general meeting (*Journ. of Ind. and Eng. Chem.*, 1915, vol. 7, 293), but which, unfortunately, has received little or no attention from our daily Press, he has clearly demonstrated that the aniline dye consumers of the United States can have all the chemists and all the dyes they want; provided they are willing to make the necessary investments of capital and to submit to the risk of uncertain profits by starting their own dye-manufacturing establishments here in the United States instead of, as in the past, favouring imported dyes, either through personal choice, or by fostering legislation which forbids the home manufacturers to utilise such methods as selling agreements, "Kartels," or other consolidation of interests, "dumping,"—so as to kill new competitors in the field, while making up the temporary loss by increasing the price of other products,—and in general, any of the many other trade arrangements and trading tricks freely and openly utilised by European manufacturers so as to stifle possible competition of our home aniline dye producers.

The outcry which has been raised as to our shortage of artificial dyes is out of all proportion if we take into consideration that the annual importation of dyes and synthetic products from Germany amounts only to about 9,000,000 dols. As our former president, Mr. A. D. Little, pointed out (*Ibid.*, 1915, vol. 7, 237) this represents about the same sum of money as the amount of candy sold annually by the Woolworth Ten-Cent Stores.

(To be continued).

METHODS OF ANALYSING VEGETABLE PARCHMENT.

THE usual method of disintegrating a sample of paper for examination of the fibrous constituents under the microscope is not readily applicable to vegetable parchment, since the fibres of the latter firmly adhere to one another and cannot easily be separated. For ordinary papers it is sufficient (Sindall and Bacon say in the *Paper Makers' Monthly Journal*) to warm a fragment of the sample gently in a weak solution of caustic soda, which is then washed out thoroughly with hot water. The paper is disintegrated by shaking in a bottle or test-tube, and is then ready for examination. Such a process fails to disintegrate vegetable parchment, and other processes have to be found by means of which the fibres can be loosened one from the other.

In 1909 Vidal proposed a process by which the external surfaces of the vegetable parchment were partly or completely removed by means of ammoniacal cupric oxide, so that the fibres in the interior of the sheet were thereby loosened and rendered suitable for examination. This method, however, is of doubtful value on account of the partial solution of some of the fibrous constituents, and while this would be immaterial in the case of a paper composed entirely of one fibrous constituent, it would be useless in a case where the vegetable parchment itself was a mixture of two fibres. The proportion of each present would probably be altered, as a solution of this character would not act equally upon two different fibres.

A method has been proposed by Bartsch, making use of

sulphuric acid as the reagent, by means of which the hard parchment is reduced to the condition of pulp. He suggests the use of ordinary sulphuric acid having specific gravity of 1.84, diluted with an equal volume of water. About 100 cc. of this diluted acid is put into a beaker and warmed to a temperature of 50° C., and small pieces of the paper under investigation are vigorously stirred with a glass rod in the warm solution of acid. The paper soon becomes spongy and gradually falls to pieces. As quickly as possible the mixture is thrown into a large beaker containing water, so that the resolvent action of the acid is at once stopped. The mass of pulp is then thoroughly washed and examined under the microscope in the usual way.

The process must be conducted quickly and in the shortest possible time, in order to prevent any serious dissolution of the fibres by the sulphuric acid. As a rule an immersion of two to five minutes is found sufficient. Should it be noticed that the cellulose appears to have been strongly attacked when observing under the microscope, a fresh quantity of paper must be treated so as to reduce the time of immersion of acid. With parchment made from rags the fibres fairly resist the action of the acid, but with wood cellulose the resistance to acid is not so great.

Bartsch appears to have made many experiments in this direction, and seems to be satisfied with the process, but it is evident that this method has the same disadvantages as that found in the process of Vidal. However carefully the operation is performed a sensible change in the condition of the fibres must take place, and probably the resultant product consists of greatly disintegrated fibre, together with a few fibres which in the case of thick papers have not been acted on by the acid. It is difficult to see how a very thin vegetable parchment, through which there has been a complete penetration by sulphuric acid in the act of parchmentising, can possibly be disintegrated sufficiently without material change in composition by such a process.

"We ourselves" (Sindall and Bacon) "prefer the little extra trouble which is necessary in order to break up the pulp by mechanical methods. For this purpose a small vertical coffee-mill answers very well. Half a grm. or less of the paper is crumpled up with hot water, then torn up into small pieces and put through the mill several times with a little water. The friction of the pieces of paper upon themselves and between the surfaces of the mill in close contact with one another reduces the paper to a fibrous condition. The pulp mass consists of fibres which are separated fairly completely, and there is no difficulty in mounting these for examination under the microscope. It is an advantage to employ the zinc chloride iodine solution in somewhat dilute form, so that the mass of pulp is only slightly stained, since the solution of ordinary strength if applied to the fibres renders them such a dense blue colour as to make them practically opaque.

"The determination of the proportion of wood cellulose in a mixture of rag and wood requires that the solution used for staining should be of the right strength, and this can be easily obtained by trial. The wood fibres in a vegetable parchment which has been well parchmentised lose many of the characteristics by which they are generally recognised when examined with the microscope."—*Paper*.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice President, in the Chair. Prof. William Arthur Bone, D.Sc., Ph.D., F.R.S., was elected a Member. The Honorary Secretary announced the decease of Lord Alverstone, G.C.M.G., P.C., M.A., F.R.S., a Member of the Royal Institution, and a Resolution of Condolence with the relatives was passed.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 27, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"A Collision Predictor." By Prof. J. JOLY, F.R.S.

The collision predictor is a mathematical instrument of simple construction. It enables the mariner when navigating in fog or thick weather to foretell risk of collision with another ship, and also the moment at which the risk is greatest. The ships concerned are supposed to be aware of each other's course and speed, and (at intervals) of their distance apart. The determination of distance is made according to principles described in a previous communication to the Royal Society. The operation of taking a reading on the collision predictor takes less than half a minute. The construction of the instrument and the principles involved cannot be conveyed without diagrams.

"Discussion of Kew Magnetic Data, especially the Diurnal Irregularities of Horizontal Force and Vertical Force, from Ordinary Days of the Eleven Years 1890 to 1900." By Dr. C. CHREE, F.R.S.

The paper is mainly devoted to a discussion of the results of measurements of the horizontal force and vertical force curves from the magnetographs at Kew Observatory for the eleven years 1890 to 1900. Subsequent to 1900 artificial electric currents diminished the value of the curves. One of the main objects is the study of the diurnal variation as given by "ordinary" days, i.e., all days with the exception of the highly disturbed. The changes of the regular diurnal variation throughout the year are dealt with in detail, and the inequalities are expressed in Fourier series. An investigation is also made of the annual inequality; for this purpose use is made of results for years subsequent to 1900 as well as of those between 1890 and 1900. The relation of the diurnal inequality to sunspot frequency is considered in the light of Wolf's formula, the constants in the formula being determined by least squares. Considerable attention is also paid to the absolute daily range or difference between the extreme values for the day. The frequency of occurrence of ranges of different size is considered in detail.

"A Portable Variometer for Magnetic Surveying." By G. W. WALKER, F.R.S.

The paper contains an account of a portable magnetic variometer for measuring horizontal force in a magnetic survey. The results obtained with it and with a Kew unifilar at forty-eight stations in the course of the magnetic survey of the British Isles in 1915 are discussed.

The operation of measuring force is reduced to a single reading of the instrument, with a reading of the temperature, at a definite instant of time, in place of the elaborate system of readings taking over an hour when a unifilar is used.

It is estimated that the normal error is not likely to exceed 5%.

"On the Single-Line Spectrum of Magnesium and other Metals, and their Ionising Potentials." By Prof. J. C. McLENNAN, F.R.S.

It has been shown that magnesium vapour traversed by electrons can be stimulated to the emission of a single-line spectrum consisting of the wave-length $\lambda = 2852.22$ A.U.

It has been shown that the absorption spectrum of non-luminous magnesium vapour contains an absorption band at $\lambda = 2852.22$ A.U., and one at $\lambda = 2073.36$ A.U.

As the lines $\lambda = 2852.22$ A.U. and $\lambda = 2073.36$ A.U. are respectively the first members of the series $\nu = 2, p_2$ 1.5, S, and ν 1.5, S—m, P, respectively, the absorption spectrum of magnesium vapour has been shown to be analogous to

the absorption spectra of the vapour of mercury, zinc, and cadmium.

The ionising potentials have been deduced for atoms of magnesium, in addition to those for the atoms of mercury, zinc, and cadmium.

Considerations have also been presented which show that if Bohr's theory affords an explanation of the origin of single-line spectra, then Frank and Hertz and also Newman must have placed a wrong interpretation on the results of their direct investigation of the ionising potentials for mercury atoms.

"The Microscopic Structure of Semi-permeable Membranes, and the Part played by Surface Forces in Osmosis." By F. TINKER.

Microphotographs of the common precipitation membranes, taken by a new method, show that such membranes are composed of small precipitate particles packed closely together, and ranging from 0.1μ to 1.0μ in diameter. Each of these precipitate particles is, however, not simple in structure, but is itself an aggregate formed by the flocculation of smaller ultra-microscopic particles. Of the membranes examined copper ferrocyanide and Prussian blue have the smallest particles.

Precipitation membranes show most of the physical properties of gels as ordinarily prepared by bulk precipitation, but they have not the same mechanical structure as the latter, the membrane having a much finer texture than the gel proper.

The pores in a copper ferrocyanide membrane range from 8μ to 60μ in diameter. Their size is such that they can block colloidal molecules mechanically, but not the ordinary crystalloidal molecules even when highly hydrated.

The order of a series of membranes with respect to pore size is the same as that of their efficiency as semi-permeable membranes. Copper ferrocyanide and Prussian blue are the most efficient membranes, and they have also the smallest pores.

There is a very close connection between the osmotic properties of a membrane and the extent to which the membrane capillaries are under the control of surface forces.

Osmotic effects are probably the result of adsorption phenomena occurring at the surface of the membrane and in the capillaries, the membrane being relatively impermeable to solutes negatively adsorbed, but permeable to solutes positively adsorbed.

"The Reduction of Metallic Oxides with Hydrogen at High Pressures." By E. NEWBURY and J. N. PRING.

Metallic oxides have been heated to temperatures of 2500°C . in dry hydrogen at pressures up to 150 atmospheres, water vapour being removed by metallic sodium.

The following oxides were reduced to metals:—

Cr_2O_3 to Cr. MnO_2 to Mn.

The following oxides were reduced to lower oxides:—

V_2O_5 to VO. TiO_2 to TiO.
 Nb_2O_5 to NbO. CeO_2 to Ce_2O_3 .
 U_3O_8 to UO_2 .

The following oxides were unchanged:—

Al_2O_3 , MgO, ZrO_2 , Y_2O_3 , ThO_2 .

The metals obtained, chromium and manganese, are probably the purest samples of these metals that have been prepared up to the present. This supposition is supported by the sharp nature of their melting-points, a feature which has not been observed with samples prepared by other methods.

"Discontinuous Fluid Motion past a Curved Boundary." By H. LEVY.

The author considers the regions in the $w(=\phi + i\psi)$ and $\Omega(=\log \frac{dz}{dw})$ planes, corresponding to the problem of the discontinuous motion of a fluid in two dimensions past

a curved boundary, and shows that the problem will be solved if the formulae can be found to transform these regions conformally into the same region in a t plane. This the author succeeds in accomplishing by a synthetic method he has devised—the vectorial superposition of rectangles in the Ω -plane. By this means it is demonstrated that the problem of the impact of a fluid against a boundary, differing by as little as may be desired from a given boundary, may be easily solved. The author pursues in fuller detail the case of symmetrical surfaces and of plane surfaces with curved ends. A few particular cases are worked out completely.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Annual General Meeting, February 2, 1916.

THE PRESIDENT, Mr. A. CHASTON CHAPMAN, delivered his Annual Address:—

Once again it is my lot to review the activities of our Society during a period of such intense and universal stress and strain as finds no parallel in the world's history. Since my last annual address was delivered the deadly struggle has continued without intermission, and if that struggle has brought untold suffering and misery to millions of our fellow-beings, there is happily some good to be placed to the other side of the terrible account.

As a nation we have in the past shown a neglect of science which has very nearly been our undoing, and although from time to time grave warnings have been uttered and powerful appeals have been made, these have for the most part fallen upon deaf ears. Now, as a result of the inflexible logic of events, the nation is beginning to realise the error of its ways, and never again can chemistry and the other experimental sciences consent to be relegated to the humble position they have so long occupied in the national esteem.

For the successful prosecution of the war, and still more for the general development and industrial protection of the country during the very difficult period which must follow the cessation of hostilities, all our best scientific brains will be needed, and all the energy and scientific organisation of which we are capable.

Among the many lessons which we are learning as the result of the war not the least important is the fact that experimental science in general and chemistry in particular is not merely an interesting intellectual occupation, but one of the foundation-stones on which national progress rests, and that its continued neglect could only lead to disaster and end in our complete defeat by more progressive and far-seeing nations.

The ignorance of the value of scientific knowledge shown by our people is very great, and unfortunately many of our rulers are little if at all better informed. As a consequence much inertia still remains to be overcome, and a great deal of leeway has to be made up. Happily signs are not wanting that we are at last directing our footsteps on the right path, and those of us who know and who have the real interests of their country truly at heart will earnestly pray that our progress along that path may be certain and rapid.

I must now pass on to a matter which has very closely concerned many of our members during the past year. I refer to the recruiting of chemists for active military service. One of the penalties which a country has to pay for unpreparedness for war—a penalty which is greatly increased by adherence to the voluntary system—is an immense waste both of human material and of treasure. Men who by their training and experience are absolutely necessary in their civil occupations for the welfare of the country both in war and in peace offer themselves and are accepted for military work which could in many cases

at least equally well performed by men who could be more readily spared.

At the outbreak of war the authorities were seemingly unaware of the vast and multifarious services rendered to the State by professional chemists and of the extent to which the welfare of the nation depended upon the adequate utilisation of their services. As a result many hundreds of highly trained chemists were to a great extent wasted by being put to military duties which could easily have been performed by men whose normal activities were of no special value to a nation at war.

This state of affairs lasted until a few months ago, when the authorities apparently began to appreciate the facts of the situation, and the Board of Trade issued a circular of instructions to local tribunals under Lord Derby's scheme, together with a "list of occupations (reserved occupations) of cardinal importance for the maintenance of some other branches of trade and industry."

Since then the Board of Trade has issued a further schedule of "reserved occupations," in which occurs the following important paragraph:—"Chemists: Analytical, consulting research chemists (not to be accepted for immediate enlistment or called up for service with the colours without the consent of the Royal Society). Chemical Laboratories: Head laboratory attendants."

It will have been noticed that chemists are not only not to be enlisted but are not allowed to enlist without the express permission of a recognised body, the only other persons in the schedule who are treated similarly being "licensed pilots, officers, and crews of vessels belonging to the general lighthouse authorities, and lighthouse-keepers"—that is to say, men whose services are absolutely essential for the public safety.

This is one of the signs of public recognition to which I referred at the commencement of my remarks, and there are indications that others will be forthcoming. It only remains in this connection to say that the President of the Royal Society has appointed a Committee to assist the Royal Society in connection with matters relating to recruiting, and that, as President of this Society, I have been invited to serve on that body.

During the past eighteen months the columns of the technical and of the general Press have been inundated with letters and with articles bewailing the neglect of chemical science in this country and deploring the want of appreciation of the services of chemists so often shown by manufacturers.

That we have shamefully neglected the claims of science is a fact of which many of us have been painfully aware for a good many years, and one which through the stern teaching of the war is gradually being brought home to the bulk of the nation. This, however, is a matter which is intimately bound up with our whole system of education, and until that system has been thoroughly reformed it is hopeless to expect that chemistry and the other experimental sciences will take their proper position.

So far as our colleges are concerned I feel very strongly that a more thorough training in analytical chemistry is desirable, and I would in addition venture to suggest that the present curriculum of those chemical students who intend to become professional chemists should whenever possible be amplified so as to include a further year of study.

During this post-graduate year the student should be trained by thoroughly competent and specially selected teachers under conditions approximating more to those of the technical than to those of the academic laboratory.

During his academic course of practical work the student is very properly taught that accuracy is the first consideration, and the factor time, which is so important in the works laboratory, scarcely enters into his calculations. Again, he has been taught to work on a small scale, has little or no knowledge of the disturbing influence of mass, and has never learned to think in terms of large scale operations. He has not, moreover, acquired even the most elementary knowledge of engineering, and

does not know how to construct or to interpret even the simplest drawings of plant.

During this additional year of study I am far from suggesting that the student should attempt to familiarise himself with any one special branch of applied chemistry, but I feel convinced that under the working conditions I have in mind he would acquire a new mental attitude and a new way of looking at chemical problems which would do much to bridge over the gap which exists at present between his academic studies and his work in the factory. Even with this additional knowledge the young chemist must, if disappointment is to be avoided, realise that he has much to learn, and that a good deal of his further technical training will have to be done at the expense of his employer.

Whilst words fail to express the indignation which one sometimes feels at the miserable wages (the word "salary" would be out of place) offered to men who have devoted several years and a not inconsiderable sum of money to their training, yet, on the other hand, the young chemist seeking a position should remember that his future lies very largely in his own hands. The chemical manufacturer is not a philanthropist, neither is he a fool. Whilst he is obviously disinclined to pay a big salary or to make a binding agreement until he knows something of the capabilities of the man he is engaging, he will be equally anxious not to lose that man's services should he prove himself thoroughly capable and useful.

Again, the manufacturer on his side must understand that in engaging the services of a young chemist from one of our universities he is getting the partly manufactured material and not the finished product. He should be told that his future employee is merely a well-trained apprentice who knows how to use the tools of his craft, but who will have to be given time in which to find his feet and to learn something of the new conditions under which he will have to work. It is here that our university professors can do much to prevent misunderstanding and disappointment by pointing out to manufacturers the limitations of the men whom they may be recommending.

A good many manufacturers—I am not, of course, referring to the heads of large concerns where many chemists are employed, and where their functions are thoroughly well understood and appreciated—do not always know very clearly what they want. They have a vague idea that some sort of chemical assistance is necessary in a modern factory, and they consequently go to one of our colleges and state that they want "a chemist." As one of the objects of our colleges is very properly to find employment for the men they have trained he is offered the services of a man who has perhaps just finished his chemical course, but who knows little or nothing of the nature of industrial chemistry or the requirements of the factory. He has done his work industriously and well, and perhaps with distinction, and his professor is obviously justified on general grounds in recommending him highly.

It is at this point, however, that the trouble to which I have alluded commences, for the young man in question is offered to the manufacturer labelled "chemist" without any qualification at all. As a very general rule no intimation is given to the manufacturer that his prospective employee is little more than a senior student, and in the absence of any statement to the contrary there is some justification for regarding him as thoroughly competent not only to carry out the routine work of the factory, but also to undertake industrial research, to cheapen production, and to effect improvements in the manufacturing processes concerned. At the end of the year in many cases nothing very definite had resulted, no additional profit had been made, and there is no obvious improvement in the factory working, and the manufacturer is very apt to give emphatic expression to his disappointment, and to inveigh against science in general and chemistry in particular.

I need scarcely say that I do not overlook the very numerous cases in which young chemists fresh from our college laboratories have entered factories and have most

thoroughly justified themselves in every possible way, nor do I desire to exaggerate in the slightest degree the extent of the difficulty to which I have referred. I have merely called attention to a state of affairs which does unhappily exist, and which, owing to its unfortunate consequences, is one for which the chemical profession should urgently seek a remedy.

I wish it to be understood, moreover, that my remarks apply especially to the general works chemists, to whom is entrusted the testing of the raw materials and finished products and the exercise of a general scientific supervision. With the more important question of industrial chemical research it is quite impossible to deal within the limits—which I fear have already been overstepped—of an annual address. I would only say that chemists competent to initiate and to carry through to a successful issue the kind of investigations which are of importance to manufacturers are comparatively speaking few in number, and that the chemical investigator, like the poet, must be born. He may be shaped, but he certainly cannot be made, and it would save not a little disappointment if it were recognised more generally on the industrial side that men possessing all the special qualities of intellect and of character which go to make a successful chemical investigator are not very frequently combined in any one man, and that the chances of obtaining the services of such a man in a more or less haphazard way, and at a salary which would be rejected with scorn by many an artisan, are not very great.

Summarising the points on which I have briefly touched in this address, I would appeal for—

1. Greater sympathy, freer intercourse, and closer co-operation between the two great branches of the chemical profession—the teachers and the practitioners.
2. The establishment of Chairs of Analytical Chemistry in our universities and colleges as a practical step towards securing the more adequate treatment of that important branch of our science.
3. The more general provision in our universities and colleges of post-graduate facilities for acquiring a good general knowledge of certain subjects which form an indispensable part of the professional equipment of every technical chemist.

The following were elected the Officers and Council for the ensuing year:—

President—George Embrey.

Past-Presidents serving on the Council—Leonard Archbutt, Edward J. Bevan, A. Chaston Chapman, Bernard Dyer, Otto Hehner, R. R. Tatlock, E. W. Voelcker, and J. Augustus Voelcker.

Vice-Presidents—H. G. Colman, J. H. B. Jenkins, and R. T. Thomson.

Hon. Treasurer—Edward Hinks.

Hon. Secretaries—P. A. Ellis Richards and E. Richards Bolton.

Other Members of Council—W. T. Burgess, J. A. Dewhirst, J. T. Dunn, P. V. Dupré, R. G. Grimwood, H. G. Harrison, E. M. Hawkins, A. W. Knapp, Stevenson J. C. G. Macadam, William Macnab, H. L. Smith, and W. Collingwood Williams.

Ordinary Meeting, February 2, 1916.

Mr. GEORGE EMBREY, President, in the Chair.

MESSRS. Thomas Featherstone Harvey, Cyril Hubert Manley, Caryl Cameron Roberts, and Frank Thomas Shutt were elected members of the Society.

A certificate was read for the first time in favour of Mr. Frank Theodore Alpe, "Bracondale," Wymondham, Norfolk.

Certificates were read for the second time in favour of Messrs. Thomas John Hitchcock and Nelson Trafalgar Foley.

The following papers were read:—

"*Note on Human Milk.*" By G. D. ELSDON, B.Sc., F.I.C.

Results of analysis, including data for the fatty portion, are given for two samples of milk taken on two successive days from the same source.

A table of figures is included for 146 samples of human milk, 67 of which were fully analysed, and 79 partial y.

"*Notes on Common Processes used in Water Analysis.*" By W. T. BURGESS, F.I.C.

The author called attention to the several little details in ordinary processes, the neglect of which causes unexpected errors in the determinations; he also dealt with the care of laboratory glass apparatus.

He stated that the green growths in condensers, which so often disfigure our laboratory benches, could be almost entirely prevented by the simple expedient of inserting a long helix of fine and bright copper wire in the water jacket, the trace of copper taken up by the water being sufficient to inhibit the development of the algæ.

The author said that he had reasons for believing that the "nitrozote" method of estimating nitrogen was not in such general use as its excellence warranted, and exhibited a slightly modified apparatus in which the determinations could be made with expedition. The ordinary measuring tube with single-bore stopcock is fitted with a large rubber "cork," of a size sufficient to take a short length of wide glass tubing which can, when required, be slipped over the stopcock and graduated part of the tube. The pressure tube is carefully selected so that its internal diameter is exactly the same as that of the measuring tube. The NO is liberated in the usual way, and when the action is completed the pressure tube is clamped so that the level of the mercury is about 40 mm. below that in the measuring tube. A few drops of distilled water are then allowed to enter the measuring tube; this water remains on the top of the turbid acid mixture, and permits the meniscus to be seen clearly. The wide glass tube is then slipped on the cork and filled with water, and after a few minutes the volume of gas and the temperature of the water-jacket are recorded. A glass or celluloid mm. scale is afterwards placed against the pressure-tube so that its zero coincides with the level of the mercury; the stopcock is then opened, and the rise of the mercury in the pressure-tube noted, and as the two tubes are of equal diameter this number multiplied by 2 gives the reduced pressure under which the gas was measured. The height of the barometer is also taken, and the weight of nitrogen may be calculated in the usual way, or preferably by the aid of the tables, &c., given in Sutton's "Volumetric Analysis."

"*Poli Oil—a New Adulterant of Ghee.*" By J. H. BARNES, B.Sc., F.I.C., and ARJAN SINGH.

The authors deal with the edible seed of *Carthamus oxyacantha*, N.O. *Compositæ*, one of the safflowers, which is found as a persistent thorny weed, growing with and alongside the wheat crop in India, from Umballa in the south to Pashawar in the north, and is difficult to eradicate.

The seeds produce poli oil, which they describe as an adulterant of ghee (the clarified butter-fat of India). The authors give the chemical and physical constants which they have determined for a genuine sample of the fresh oil, and state that the analyst will have little difficulty in recognising the adulterant when found in conjunction with ghee.

CHEMICAL SOCIETY.

Ordinary Meeting, January 20, 1916.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society through death of Messrs. Frank Buckley, Heinrich

Debus, Edmund Foster Hudson, and the Right Hon. Sir Henry Enfield Roscoe.

The PRESIDENT, in announcing the deaths of Dr. Heinrich Debus and of Sir Henry Roscoe, said that in them we had lost two of our senior Fellows, both pupils of Bunsen, each of whom in his own way had been an eminent teacher of chemistry for about forty years. Dr. Debus had contributed to the Transactions in his eightieth year (1904). Sir Henry Roscoe, besides practically founding the Manchester School of Chemistry, had done more than any one man in this country for chemistry and chemical education by his writings, speeches, services on Royal Commissions, and otherwise. He was happy in living to see the ample fruition of his labours. The Society is fortunate in possessing such a lifelike presentment of him as that in the Library.

Mr. B. B. Dhavale was formally admitted a Fellow of the Chemical Society.

The PRESIDENT reminded Fellows that at the next Ordinary Scientific Meeting, on February 3, Prof. W. H. Bragg, F.R.S., would deliver a lecture entitled "The Recent Work on X-Rays and Crystals and its Bearing on Chemistry."

Certificates were read for the first time in favour of Messrs. Ralph Hall Atkinson, B.A., West Shaws, Barnard Castle, Darlington; Thomas James Bandinel, 104, Trinity Rise, Tulse Hill, S.W.; Christopher Barber, 60, Harcourt Road, Sheffield; Kakuji Goto, University College, London; Claude Saville Grace, B.Sc., 36, Harvard Road, Gunnersbury, W.; Frank Nettleton Harrap, M.Sc., 12, St. Mary's Place, Bury, Lancs.; Albert Francis Huggins, Cartref, Cromford Road, West Bridgford, Nottingham; Arthur Moore, B.Sc., 199, Windsor Road, Oldham; John Walter Hyde Oldham, B.A., Trinity College, Cambridge; Sidney Radcliff, Dunheved, Alexandra Street, Hunters Hill, Sydney, N.S.W.; John Read, M.A., Ph.D., B.Sc., University Chemical Laboratory, Pembroke Street, Cambridge; Guy Thomas Percy Tatham, B.Sc., 120, Lower Baggot Street, Dublin.

The following certificate has been authorised by the Council for presentation to ballot under By-Law I. (3):—James Russell Downie, Southern Explosives Company, Weston, N.S.W., Australia.

The following papers were read:—

"The Action of Water on Cupric Thiocyanate." By JAMES CHARLES PHILIP and ARTHUR BRAMLEY.

"A New Synthesis of Histidine." By FRANK LEE PYMAN.

NOTICES OF BOOKS.

Catalysis and its Industrial Applications. By E. JOBLING, A.R.C.Sc., B.Sc., F.C.S. London: J. and A. Churchill. 1916.

The text of this book originally appeared as a series of articles in the *Chemical World*, from which it has been reprinted with very little alteration. Technical students and industrial chemists will find that it contains an interesting survey of a subject which is of great practical importance. Some account is given of the general characteristics of catalytic reactions, and then carefully chosen examples of such reactions are discussed in some detail, beginning with the manufacture of sulphuric acid by the chamber and contact processes respectively. The explanations of the theory of these reactions are well up-to-date, and modern modifications of practice are described. The preparation of chlorine by the Deacon process, the Hargreaves-Robinson process for salt cake, and the Claus-Chance process for the recovery of sulphur from alkali waste are described, and a comparatively long chapter is devoted to commercially successful methods of fixing atmospheric nitrogen. A short account is given of the catalytic influence of hot surfaces on chemical reactions. Hydro-

genation by catalytic methods is treated with the fulness its growing importance warrants, and the work of Sabatier and his collaborators on dehydrogenation and oxidation is also discussed. Finally, the use of catalysts in dehydration, hydrolysis, saponification, &c., is treated in outline in the last chapter.

The British Dominions Year Book, 1916. London: The British Dominions General Insurance Co., Ltd.

THE articles in this year book deal with the subjects which are most engaging attention at the present moment, such as the cost of the war, international law in the present war, the economic outlook for Germany, aircraft as belligerents, &c. They have all been written by men who have special knowledge of their subjects and are qualified to write authoritatively. Special attention may be drawn to the article of Sir Leo Chiozza Money on "A Business-like Empire," in which the necessity for utilising and developing the Empire's resources is emphasised, and to another on "British Opportunities in Russia," by Mr. Louis A. Rojansky, which contains a highly instructive table of imports to Russia from Germany, Austria-Hungary, and the United Kingdom. The Year Book will not be published in the ordinary way, but will be presented to the public and to business men or women who are interested in the development of the Empire.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Royal Society of Arts, 4.30. (Fothergill Lecture). "National and Historic Buildings in the War Zone—their Beauty and their Ruin," by the Rev. George Herbert West, D.D.

Biochemical Society, 5.30. (At the Institute of Physiology, University College, London). "Effect of Temperature on Inhibition of Enzyme Action," by W. M. Bayliss. "Analysis of Proteins—I., The Estimation of Arginine by Decomposition with Alkali," by R. H. A. Plimmer. "Preparation of Cholesterol," by W. W. Reeve.

TUESDAY, 15th.—Royal Institution, 3. "Nerve Tone and Posture," by Prof. C. S. Sherrington.

Institution of Petroleum Technologists, 8. "Oil Shales, especially those of Dorsetshire," by W. H. Manfield.

WEDNESDAY, 16th.—Microscopical, 8. "Progress and Development of Vision and Definition under the Microscope," by Messrs. Heron-Allen, Earland, and Rousselet. "An Experiment with the Ultra-microscope," by J. E. Barnard.

THURSDAY, 17th.—Royal Institution, 3. "Measurement of the Brightness of Stars—Variable Stars," by Sir Frank Watson Dyson.

Royal Society of Arts, 4.30. "The Saints of Pandharpur," by C. A. Kincaid.

Royal Society. "Action of Cobra Venom," by A. R. Gushny and S. Yagi. "Gametogenesis and Sex Determination in the Gal-fly (*Neuroterus leucocarpus*)," by L. Doncaster. "Structure and Development of the Skull and Laryngeal Cartilages of Perameles, with Notes on the Cranial Nerves," by P. C. Esdaile. "Physiological Investigations with Petiole-Pulvinus Preparation of Mimosa-Pudica," by J. C. Bose and S. C. Das.

Chemical, 8. "Simultaneous Estimation of Carbon and Bromine by the Chromic Acid Method," by P. W. Robertson. "Relation of Position Isomerism to Optical Activity—Part X., The Menthyl, Alkyl Esters of 3- and 4-Nitrophenic Acid, &c.," by J. B. Cohen, D. Woodroffe, and L. Anderson. "New Reaction of Semicarbazide Hydrochloride," by E. E. Turner. "A Product of Natural Indigo Manufacture," by A. G. Perkin. "Action of Sulphuric Acid upon Alloy Steels," by L. Aitchison. "Additive Compounds of s-Trinitrobenzene with Heterocyclic Compounds containing Nitrogen in the Ring," by S. G. Sastry. "Study of Binary Mixtures—Part II. Densities and Viscosities of Mixtures containing Substituted Phenols; Part III. Freezing-point Curves; Part IV. Heats of Reaction and Specific Heats," by A. Bramley.

FRIDAY, 18th.—Royal Institution, 5.30. "Polarised Light and its Application to Engineering," by Prof. E. G. Coker.

SATURDAY, 19th.—Royal Institution, 3. "Eminent Generals of the last Great War—Sir Ralph Abercromby and Sir Charles Stuart," by Hon. J. W. Fortescue.

THE CHEMICAL NEWS.

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SOME POINTS CONNECTED WITH THE REPRESENTATION OF THE BENZENE FORMULA.

By GERVAISE LE BAS, B.Sc (Lond.).

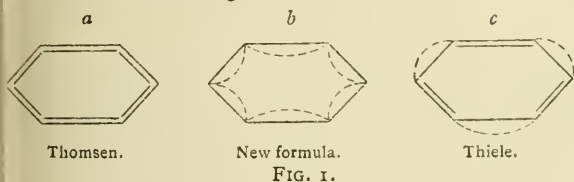
IN the CHEMICAL NEWS (1915, cx., 37) the various benzene formulæ were arranged in two classes—

- (a) the mobile valency type, and
- (b) the fixed valency type.

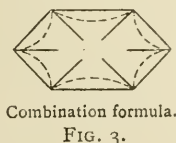
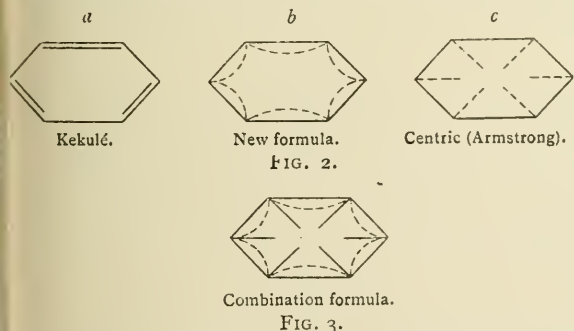
Moreover, another formula was suggested, based on a regularity shown by the molecular heats of combustion of various aromatic compounds. This, as was shown, seems to be connected with two others, in form at any rate (Fig. 1).

These three formulæ are fundamentally the same, and are different methods of stating what becomes of the fourth valency of the carbon atoms in benzene. The idea which has to be shown is the combined unsaturation and stability of the benzene molecule. The first two are different methods of stating the fact that the fourth valency, or rather the force involved, is equally distributed between the carbon atoms. The third, which preserves the Kékulé idea of three ethenoid linkages, shows the residual affinity compensated in the three regions indicated. The molecules are thus unsaturated yet stable.

The new formula will also be found to be fundamentally connected with another two in a different way. Such a series is shown in Fig. 2.



Numbers *b* and *c* (Fig. 2) may be combined in what may be called a "combination formula," and this would express more than any one formula would do (Fig. 3).

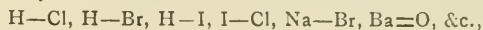


Not only does this combination formula involve the two formulæ mentioned, but it also suggests the possibility of Kékulé's formula.

In the above form it is, however, incomplete, and read in a certain way may be untrue, even as the centric formula may be untrue if read in this way. Even so, an error has persisted in the literature of the subject and in text-books,

which is that all the free valencies are directed inwards. This is not the case.

The reason is found in the probable difference existing between the valencies of individual atoms. Some difference of a fundamental character must exist or combination could not occur. The possibility of combination is easily understood in—

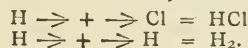


for positive and negative elements are united, but it is not so apparent in—



It is clear that whatever be the cause and mechanism of the combinations, a similarity exists between those of class one and those of class two.

The point of view from which we find it convenient to regard the matter is that of force. We may suppose that from the *positive* valency there is an *outwardly* directed force, and from the *negative* valency an *inwardly* directed force. The formation of hydrochloric acid and gaseous hydrogen from their elements may thus be represented.



This indicates that the two atoms of hydrogen are not in the same condition; one is, in fact, positive and the other negative. The modern electronic theory would no doubt explain the matter more elaborately, but a recognition of the above feature is all that is necessary (Fig. 4).

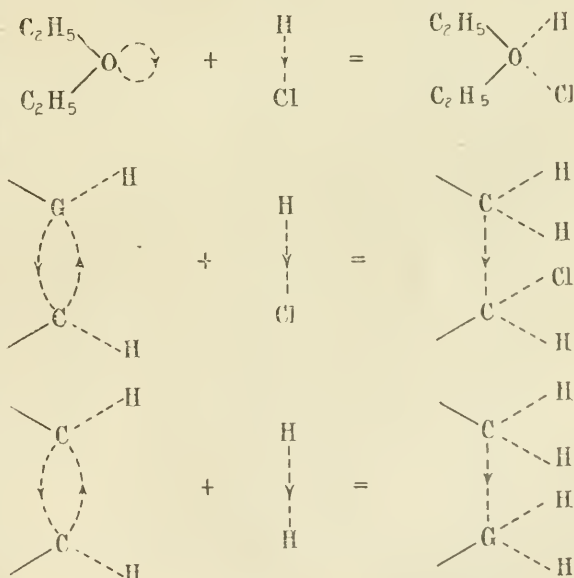


FIG. 4.

Not only in such simple combinations is such a hypothesis necessary, but also in more complicated unions. The manner in which additive reactions occur in organic chemistry is no doubt to be explained by some such fundamental property of matter like the above.

We cannot believe that the condition of things is different in the two last cases. The principle involved needs special emphasis, as probably it has not received sufficient recognition in recent chemical literature. Such neglect may easily give rise to misconception and error, or cause them to persist. One such mistake at any rate is found in connection with Armstrong and Baeyer's centric formula, which is that the forces are supposed to be directed inwards. This would make such vibrations as do occur impossible. The suggested modification is embodied in

Fig. 5. On this assumption, the combination formula can also be modified.

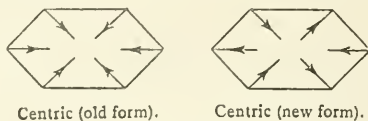
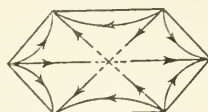


FIG. 5.



Combination formula.

FIG. 6.

It is now easy to understand why, by the additional assumption of vibrating valencies, we find it possible to regard the centric formula as an intermediate phase of the vibration between two extreme phases, represented by the condition of things in the two alternative Kékulé formulæ (Fig. 7).



FIG. 7.—DIAGRAM REPRESENTING THE PHASES OF THE VIBRATIONS IN THE BENZENE MOLECULE.

It will be seen that the combination formula involves all three. Regarded from the static point of view this formula resembles the field of force shown by six magnetic poles arranged in a ring, three positive and three negative—the negative and positive alternating. The forces are directed outwardly from the positive poles and inwardly in the case of the negative poles. The formula suggested in a former number of the CHEMICAL NEWS (*loc. cit.*), and referred to at the beginning of this paper, is to be regarded as a subordinate part of this field. Viewed dynamically the different parts of the diagram shows the disposition of the "free" valencies at different phases of the vibration, and thus at different times. Regarded in this light it would thus be a synthetic formula embodying the condition of things in the three separate formulæ afterwards shown. It becomes a matter for consideration whether there is any interaction between the valencies in the para position, so that the centrally directed linkages might resemble the linkages in the diagonal formula of Claus. This is probably not so, but there might be interaction nevertheless, so this can be represented by completing the diagonals by dotted lines. The other formulæ all contain errors in principle or are faulty representations of facts.

The singly linked formulæ, Claus's diagonal formula, Baeyer's prism, hexagonal formulæ, and others of a similar character are open to objections which need not be enlarged upon.

Thiele's formula is correct for the most part in principle, but like the new formula is incomplete. It is, however, on other grounds objectionable. The reason is that it retains the error involved in the double bond representation of the ethenoid linkage $\equiv$. The latter leads us to suppose that the second bond is similar to the first, and that thus the ethenoid linkage is twice as firm as the single one.

This is not the case. If we consider the fourth valency to represent the greater part, if not the whole of the free energy connected with the individual carbon atom, and that this free energy is neutralised in a manner consistent with the symmetrical character of the molecule, that is, equally distributed between the carbon atoms, the idea is no doubt better represented by the new formula than by that of Thiele. It should be remarked that the new

formula retains Thiele's conception of partial valency. Both, however, are incomplete.

The formulæ best worth preserving are probably the combination formula which is more complete than any one, and the set of three made up of Kékulé's two alternative formulæ and the corrected centric formulæ.

A SIMPLE METHOD FOR VAPOUR-DENSITY DETERMINATIONS.*

(PART XII.).

By PHILIP BLACKMAN.

IN the *Zeitschrift für Physikalische Chemie*, 1909, lxx., 549, was described a method whereby the author's apparatus could be used with substances which give dark coloured vapours and yet enabled the manometer to be read. This difficulty is more easily overcome by having the manometer not inside, but *outside*, the bulb.

A piece of wide glass tubing, to act as the bulb, of length consistent with the heating apparatus, has at one end sealed on to it a piece of capillary tubing, the open end, A, of which (Fig. 1) is then sealed. A thread of mercury, A, is then introduced into the capillary 2 or 3 cm. from the bulb. (This is easily effected by pouring a drop

RESULTS.

RESULTS.							Vapour-density.	
w.	l.	t ₁ .	p.	V.	L.	L _c .	Found.	Theory.
Grm.	Mm.	°C.	Mm.	Cc.	Mm.	Mm.		
CH ₃ I.								
0.3888	181	15.5	758	102.3	294	297	70.84	70.93
0.4046	174	16.0	760	99.3	290	294	70.77	70.93
0.3852	171	16.0	760	96.8	283	285	71.01	70.93
0.3852	167	16.0	759	94.0	280	282	70.90	70.93

C₂H₅I.

0.2677	190	16.0	758	90.8	279	283	72.10	77.92
0.2784	181	16.0	758	87.8	274	276	72.10	77.92
0.2534	180	16.5	759	81.2	271	273	72.12	77.92
0.2519	179	16.5	759	80.0	269	273	72.11	77.92
0.2707	169	16.0	760	76.0	266	269	72.09	77.92

C₂H₅Br.

0.2918	170	16.5	754	121.9	259	263	53.00	54.48
0.3007	165	16.5	759	119.6	256	259	52.91	54.48
0.2763	163	17.0	759	111.8	252	254	52.96	54.48
0.2658	160	16.5	765	105.7	248	250	52.99	54.48
0.2549	158	17.0	766	99.1	245	250	53.02	54.48
0.2236	158	17.0	767	94.0	240	242	52.99	54.48

CH₃.OH.

0.2354	80	17.0	767	90.5	236	241	15.50	16.00
0.2994	76	17.0	767	87.3	232	236	15.50	16.00
0.2572	70	16.5	765	84.5	230	236	15.48	16.00
0.2656	65	16.5	765	80.1	228	230	15.49	16.00
0.2607	64	16.0	759	78.0	226	230	15.51	16.00
0.2610	60	16.0	758	73.2	220	226	15.50	16.00
0.2454	60	15.5	759	71.1	217	220	15.50	16.00
0.2461	55	16.0	759	65.6	210	212	15.50	16.00

C₂H₅.OH.

0.2447	100	16.5	750	120.5	205	208	22.88	23.00
0.2369	98	16.0	753	117.0	200	203	22.87	23.00
0.2197	98	16.5	755	110.9	198	200	22.89	23.00
0.2424	90	17.0	753	105.4	197	200	22.90	23.00
0.2431	87	17.5	756	101.1	194	199	22.87	23.00
0.2403	84	17.0	759	96.2	191	195	22.91	23.00
0.2184	85	16.5	757	93.3	187	190	22.88	23.00

* Continued from *Journal of Physical Chemistry*, 1911, xv., 871; CHEMICAL NEWS, 1909 c., 174.

RESULTS (continued).

w.	l.	t ₁ .	p.	V.	L.	L _c .	Vapour-density.	
							Found.	Theory.
Grm.	Min.	°C.	Mm.	Cc.	Mm.	Mm.		
(C ₂ H ₅) ₂ O.								
0.3115	88	16.5	757	90.1	185	188	36.73	37.00
0.2978	87	16.5	757	87.3	182	184	36.74	37.00
0.3311	81	17.0	759	86.3	180	183	36.77	37.00
0.2875	83	17.5	760	80.9	177	180	36.72	37.00
0.2522	85	16.5	760	77.2	174	175	36.72	37.00
0.2669	80	16.5	760	74.5	171	174	36.72	37.00
0.2397	82	16.5	760	71.6	169	172	36.74	37.00
0.2395	80	16.5	760	69.8	167	170	36.75	37.00

CH₃.CO₂.C₂H₅.

0.3294	130	16.5	758	150.3	200	205	46.20	44.00
0.3051	125	16.5	758	147.8	200	207	46.25	44.00
0.3612	120	16.5	757	142.1	196	200	46.23	44.00
0.2882	126	17.0	757	139.1	190	195	46.22	44.00
0.2952	121	17.0	757	135.4	187	190	46.22	44.00
0.2970	115	17.5	759	130.2	180	184	46.22	44.00
0.2239	119	17.0	758	126.0	170	175	46.20	44.00
0.1550	127	17.0	759	121.5	165	170	46.21	44.00
0.1670	120	16.5	760	116.9	161	165	46.22	44.00
0.1532	120	16.5	760	112.9	158	163	46.25	44.00
0.1410	118	17.0	759	109.9	154	158	46.22	44.00

(CH₃)₂CO.

0.2129	80	17.0	749	100.1	150	153	28.60	29.00
0.2191	76	17.5	749	96.5	147	150	28.61	29.00
0.1648	82	17.5	751	90.4	142	147	28.61	29.00
0.1534	80	18.0	750	87.3	138	140	28.61	29.00
0.1681	74	18.0	754	84.0	135	137	28.60	29.00
0.1334	78	16.5	753	81.0	129	133	28.59	29.00
0.1533	70	16.0	766	76.9	124	130	28.59	29.00
0.1634	65	15.5	767	74.1	120	127	28.60	29.00
0.1309	69	15.0	761	70.2	118	125	28.61	29.00
0.3089	47	16.0	758	66.3	102	107	28.61	29.00
0.1709	48	17.5	756	64.2	99	104	28.61	29.00
0.2063	40	17.0	760	60.0	95	100	28.60	29.00
0.2965	109	18.0	760	155.1	191	200	28.59	29.00
0.3105	103	17.5	760	152.3	187	193	28.60	29.00
0.3829	90	18.5	760	149.1	183	190	28.59	29.00
0.3295	94	15.0	758	143.8	180	185	28.60	29.00
0.2980	96	15.0	758	138.6	177	185	28.61	29.00
0.3276	86	15.0	749	131.1	172	180	28.58	29.00
0.2955	88	17.0	753	124.5	171	180	28.59	29.00
0.2480	81	18.0	766	120.8	165	170	28.60	29.00

CH₃.CN.

0.2697	75	16.5	759	116.0	160	164	23.80	20.52
0.2908	71	16.5	759	114.2	160	164	23.17	20.52
0.2637	73	17.0	756	112.3	158	160	23.78	20.52
0.2677	70	17.5	756	110.0	156	159	23.78	20.52
0.2986	65	17.0	756	106.0	156	158	23.80	20.52
0.3056	64	18.5	758	105.3	156	159	23.81	20.52
0.3242	60	18.0	758	102.9	154	156	23.79	20.52
0.3218	60	18.0	759	100.0	153	157	23.82	20.52
0.3407	55	18.0	763	96.4	150	155	23.80	20.52
0.3433	54	18.0	763	95.2	148	150	23.80	20.52
0.2877	57	17.5	763	90.1	146	150	23.78	20.52
0.2887	54	17.0	763	88.1	140	145	23.80	20.52
0.2613	55	16.5	763	85.1	136	140	23.81	20.52
0.2653	51	16.5	766	80.3	134	139	23.78	20.52
0.2378	52	16.0	760	78.3	130	135	23.79	20.52
0.2518	48	17.0	760	76.4	125	130	23.79	20.59
0.2160	49	17.5	760	72.1	120	126	23.77	20.52
0.1801	51	18.0	754	69.3	116	120	23.78	20.52
0.1714	50	18.5	756	65.4	113	120	23.81	20.52
0.1915	43	18.0	758	60.3	110	115	23.82	20.52

apparatus is placed with the capillary tube horizontal, and the length, *L*, of the air-thread is measured. The body to be experimented on is weighed out (weight *w*) in a small tube and placed in the bulb, the open end of which is then sealed up. When the bulb has cooled down to the external (room) temperature, *t*₁ °C., it is placed horizontally and the length, *L*_c, of the manometric air-thread is measured (Fig. 2), and the external (room) atmospheric pressure is noted. The whole is now heated in a horizontal position



FIG. 1.

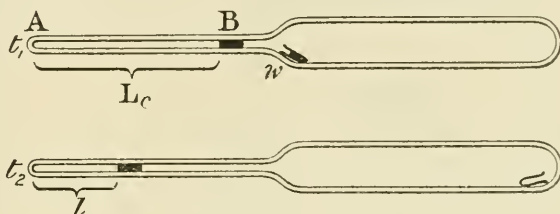


FIG. 2.

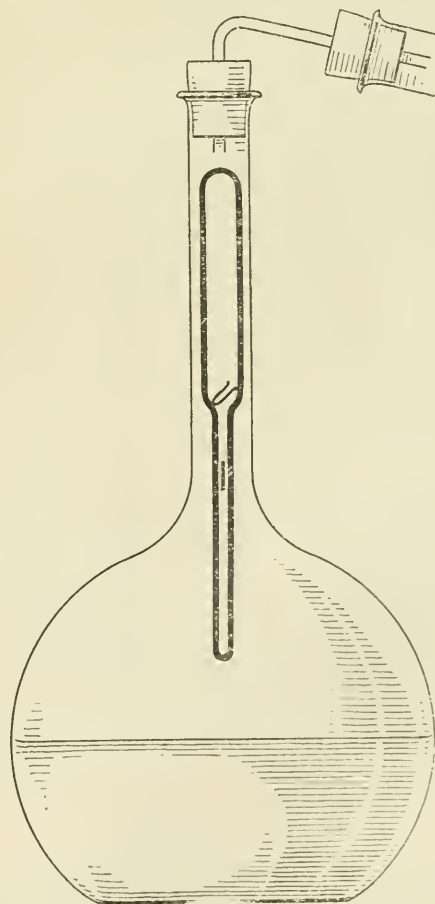


FIG. 3.

of mercury into the bulb, A being vertically downwards, and heating the capillary to cause some of the air to escape, and, on cooling, the mercury enters). The

in a suitable vessel to a temperature, $t_2^\circ \text{C.}$, sufficiently high to cause the substance to completely vaporise and the length, l , of the air-gauge is measured. The vapour-density is calculated from the formula—

$$\frac{31068 w l L_c (273 + t_1)}{p L V (L_c - l)}$$

The bulb may be heated in a vertical position; for instance, suspended above the liquid in its vapour in a wide-necked flask, in which case if the mercury thread exerts a compressing force upon the air in the manometer (Fig. 3) a correction for l must be made, given from the formula—

$$\frac{1}{l} = \frac{1}{l_c} + \frac{M(273 + t_1)}{p L (273 + t_2)}$$

(M = the length of the mercury thread and l_c = the manometric air-thread length at t_2°), and if the mercury-thread produces an extending force upon the air in the

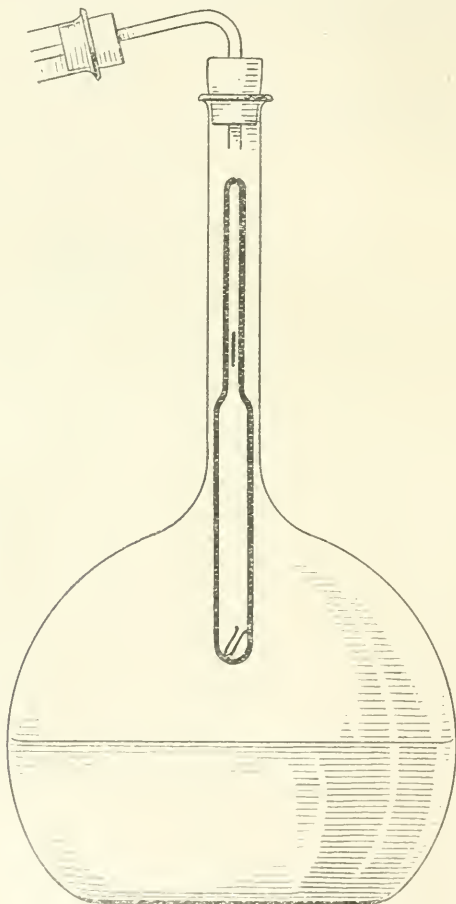


FIG. 4.

manometer (Fig. 4) the correct value for l must be calculated from the formula—

$$\frac{1}{l} = \frac{1}{l_c} - \frac{M(273 + t_1)}{p L (273 + t_2)}$$

(See *Journ. Phys. Chem.*, 1903, xii., 668, for the deduction of these formulae).

(To be continued).

APPLIED CHEMISTRY.*

By L. H. BAEKELAND.

(Concluded from p. 68).

Local Opportunities of American Chemical Industries.

THE development of any chemical industry is a matter of local opportunities; for instance, the manufacture of cellulose, as well as the industry of wood distilling, have taken a greater development in the wood-covered sections of the United States than in Germany or any other country in the world.

The magnitude and earning capacity of the largest German chemical enterprises, however imposing they may be, look less astonishing if you take into consideration that some of these companies have been in existence for more than half a century. Much younger American chemical enterprises, which make American specialties—for instance, the Eastman Kodak Company, which sends its films and photographic papers throughout the whole world—have annual earnings decidedly greater than the most successful German chemical works of much older existence. Nor is the value of the output of our largest purely chemical companies much less important than that of the German concerns.

Sulphuric Acid.

This country is now the greatest producer of sulphuric acid with an annual production of about 3,000,000 tons. Yet it is not so long ago that the first maker of sulphuric acid could not even find a purchaser for a trifling small production of a few tons per week. It needed the opportunity of a home market; by and by this was created by the refining of petroleum after the discovery of our oil fields, the discovery of natural phosphates and the resultant industry of superphosphates, the use of dynamite for blasting, the development of the glucose industry, and electrolytic copper refining. These and many other new industries all required large amounts of sulphuric acid, and gave this country an opportunity of developing sulphuric acid manufacturing to its present importance. In fact the same reasoning holds good for all of our industries. I doubt very much whether the talented foreigners, who have now become proficient in chemical manufacturing, would have tried their initiative and enterprise by specialising in coal-tar dyes manufacturing if they had had the limitless opportunities of an immense undeveloped country like ours, to which to give outlet to their spirit of pioneership in mining, transportation, agriculture, and similar subjects, all beckoning for more urgent attention, and offering at the same time more immediate rewards.

American Electrochemical Industries.

In the meantime some of our other chemical industries, better suited to our local conditions, have taken such an enormous development here as to make the United States an undisputed leader in at least some of them. Such products as the various acids and salts, aluminium, artificial abrasives, soda and caustic alkalis, bleaching powder, chlorine products, electrolytic copper, are decidedly more important in value and in economic importance than the few million imported coal-tar dyes.

Mr. F. A. Ladbury (*Metallurgical and Chemical Engineering*, 1915, xiii., 277) pointed out rightly that if there had been a shortage in some of the products of our electrochemical industries, in which the United States has been a pioneer, the consequences to our national economics would have been so serious that the present complaint of our aniline dye users would have sounded like a timid whisper compared to the bellowing lamentations of so many more important industries which would

* Presented at the fifty-first Meeting of the American Chemical Society, Seattle, August 31 to September 3, 1915. From the *Chemical Engineer*, 1915, vol. xxii., No. 6.

have become absolutely paralysed. The fact is that few men realise how many industries are directly dependent on the work of American chemists. If the aniline dye industry has been somewhat neglected in this country there are many other good reasons for it. Not only was the possibility of reasonable profits too scant to offer special inducement to clever-headed business men to risk their capital in this branch of manufacturing when they had so much better choice in other channels of enterprise, but the first raw material, suitable coal-tar, was not abundantly available here as it is in Europe, for the simple reason that this country long ago discarded the older and more expensive methods of gas manufacturing generally used in Europe, and which give coal-tar as a by-product. The less expensive and simpler water-gas process adopted in the United States gives no suitable gas-tar; it is only of late, by the introduction of the by-product coke ovens, that we can look forward to an almost unlimited supply of coal-tar.

In the meantime the German manufacturers had every opportunity in specialising in these coal-tar industries and could afford to concentrate their efforts so as to supply not only their home consumption and that of the United States but that of the whole world; in about the same way as the United States sends to the remotest corners of the globe its sewing-machines, its typewriters, and its Ford cars.

Judging from the past history of the chemical industry in America I have little doubt that the day it will be found profitable to manufacture all kinds of synthetic dyes here in the United States, instead of a few, as is the case now, there will be little further delay in supplying the demand by a hustling and bustling home production.

In fact it is quite possible that under present abnormal conditions this branch of manufacturing may be stimulated to the point as to result in over-production after the war is over.

Chemical Research in United States.

If hitherto our chemists have been deficient in this special line we can with some satisfaction point to better efforts in other chemical industries. For instance, it is not sufficiently known how many research chemists in our different American manufacturing establishments are busily occupied in studying and improving manufacturing processes, nor what large sums of money are devoted every year to industrial chemical research. If we hear it constantly repeated that some of the largest German chemical companies have hundreds of chemists and engineers, it is less known that right here in the United States the number of chemists employed in some of our better organised chemical enterprises is scarcely less, but nobody finds it necessary to boast about it; in fact the most striking symptoms is that so many engineering enterprises, for instance, some of our large electrical companies—although their field of action seems rather remote of chemical subjects—have now elaborate chemical research organisations, of which the record is well known by their excellent results.

Conditions were quite different some fifteen or twenty years ago, but this country has grown, and as the requirements and opportunities grew up at the same time new chemical problems arose thereby.

The Analytic and Constructive Turn of Mind.

The urgent nature as well as the magnitude of some of these new chemical problems is shaking our chemists awake—is making new men of them.

Prof. Whitaker is probably right when he says that the chemists are thirty years behind the engineers as far as method and attitude of mind is concerned, but this same criticism holds good for chemists all over the world. The fact is that the engineer was called first, and he was born centuries before the chemist, but the latter is now making up for lost time.

New conditions, new problems are compelling the chemist to learn to tackle a proposition in a true engineering spirit, and to hit some business sense to it. He is learning to forget thinking or acting on the test-tube plan; he is thrown more and more in contact with business men; he begins to realise that too one-sided theoretical considerations are sometimes more dangerous than complete ignorance, and that a sense of proportion and relative values is the first requirement for good practical effort.

Here indeed is one of the weakest spots of the chemist. Aside from the fact that the chemical profession seems one of those vocations which have fascinated a large number of intellectual freaks, it has generally attracted men of an analytical rather than a constructive turn of mind. Successful engineering is essentially constructive. The most urgent work for the chemist of to-day must be constructive; he must learn how to cement together the vast amount of data which already lie at his disposal even if he himself has to provide this very cement by further research.

The Chemist in Other Industries.

The chemist of to-day is no longer confined to purely chemical enterprises. Even the most stubbornly conservative manufacturers have learned through competition that every industry, however mechanical be its nature, has its chemical problems. Things have changed rapidly since the day Andrew Carnegie listened with a sly twinkle in his eyes to the fun his competitors were poking at him when he first engaged a spectacled professor to investigate the chemical problems in his ironworks. Conditions have now become reversed; to-day a steel or iron works without a competent chemist justly provokes contempt and distrust.

Nor is the time so far distant when even our biggest railroads had not begun to realise how they missed the constant services of a staff of chemists so as to advise them in the endless chemical problems which present themselves in the operation of a well-organised railroad.

Some time ago I visited the plant of the National Cash Register Company in Dayton, Ohio. One of its most interesting departments was its well-equipped chemical laboratory, where no end of chemical questions relating to the manufacture of purely mechanical devices have to be studied and solved.

No up-to-date motor-car works is complete without its chemical department, and the same remark holds good for all well-organised engineering concerns.

In this country the importance of chemistry has been first appreciated in its relations to agriculture. So obvious was this that we set an example to all other nations of the world by the number of our Federal and our State chemical agricultural laboratories. This more than anything else was the entering wedge of applied chemistry in this country, which extended later on in the Government service, Geological Survey, Bureau of Standards, and the Bureau of Mines. Nor did the useful effect stop there. Many of our Federal chemists, our State chemists, have left public service to accept better-paying positions in private industries, but the men trained in public service implanted their high aims and scientific ways in some of our commercial enterprises, which needed it badly. I know of some cases where this beneficial influence changed radically the whole spirit of the commercial organisation from its manufacturing to its selling department, and introduced, instead of reckless, sordid commercialism, a spirit of fairness and efficiency which soon proved the more profitable policy.

Ethics of the Chemist.

In this and similar directions the chemist can exercise a valuable moral influence on the community. If you think it over you will find that the quest of efficiency lies quite close to the path of honesty, justice, and equity.

Here also the chemist has much to learn. In some instances I have been astounded at the almost childlike attitude of mind of some of our chemists, who are too ready to sell their services to anybody who has a temporary use for them, irrespective of the underlying motives or purposes.

Some lawyers tell me that they never have the slightest difficulty in hiring chemical experts to defend contradictory opinions. It is quite amazing how some chemists in their eagerness of pleasing their employers will overlook their own ignorance of the most elementary principles of patent law, as well as their superficial acquaintance with the many details of intricate technical questions, while not hesitating to furnish cocksure opinions which encourage infringers or industrial pirates to trespass on the rights of intellectual property of others. Much ruinous patent litigation would be avoided in this country and invention would be better encouraged if we had more men of the type of a well-known British electrical expert, who never hesitates in court to tell the simple and direct truth, regardless whether it kills or saves the case of his client. His statements are so highly valued and respected that the judges accept them without suspicion, and the same expert is frequently retained by the two opposing parties, whom he serves impartially, and who gladly pay him higher fees than to a mere litigation-acrobat-expert or a chemical "ambulance-chaser."

Employers and Employees.

The ethics of our profession have been dealt with by the American Institute of Chemical Engineers, and have been embodied in its recently adopted Code of Ethics, which may furnish a good guide for younger or less experienced chemists. And this leads me to state that many more manufacturers or business men would be induced to utilise the services of chemists if they could feel confident that in so doing they are not putting themselves at the immediate mercy of a stranger by confiding to him facts or processes which it has cost them many sacrifices of time and money to accumulate, and the undivided knowledge of which constitutes sometimes one of their most valuable assets. On the other hand, a chemist can hardly be of any service unless his client or employer is just as frank with him as he would be with his lawyer or physician. However, this mooted point is easily overcome by referring to the Code of Ethics to which I have just alluded, or, better, by making a preliminary agreement between the chemist and his client or employer, safeguarding the interests of both parties. But in such a case the compensation to the chemist should be made commensurate to the occasion.

This same principle holds good in the employment of chemists in manufacturing plants, where the chemist is either engaged in research or in a manufacturing capacity. An employer should not expect an intelligent chemist to render him important services without proper compensation, and in as far as the practical value of the work of a chemist can seldom be determined in advance, it will pay the employer to offer special inducements or rewards for initiative. He can well afford to give his chemist some share of the increased profits he has received through his work; to do otherwise would be narrow-minded, short-sighted, and detrimental to the direct interests of the employer. The work of a research chemist cannot be performed nor measured like that of a bookkeeper or a labourer; the results of his work are uncertain; delays and obstacles beset him at every turn; sometimes luck plays an important role; but goodwill, enthusiasm, and persistent endeavour are indispensable factors, and these may be encouraged or killed by the attitude of the employer. An employer who is unfair, or who cannot arouse the respect or the enthusiasm of his chemists, cannot get the best there is in them. He must make them feel that if their work turns out well for him they will get some decent share of compensation; therefore a reasonable

salary ought to be supplemented by the possibility of a bonus or some share in the profits based on the earnings brought about directly by the work of the chemist.

On the other hand the chemist must not overlook the financial sacrifices and business risks assumed by his employer. He should specially bear in mind that knowledge or experience gathered at great cost by his employer or through expensive factory equipment or other facilities have in most cases enabled him to take up his own work at an advanced stage. It would be rather unfair, unless otherwise stated, that a chemist should be allowed during or after his period of employment to divulge or take advantage of all knowledge or information gathered around the plant in which he is engaged, or patent for his exclusive benefit any inventions he may make on those particular subjects for which he is engaged as long as the stimulating ideas themselves have been gathered by the very means put at his disposal by his employer. All these questions should be provided for and embodied in an equitable contract, which will necessarily vary with special circumstances. But here again niggardiness or too great cunningness of the employer will hardly pay. Unless his chemist be a fool—and a fool of a chemist is not worth anything—he will lose the goodwill and confidence of the very man whose work is primarily dependent on these factors.

Faithful and generous observance of these conditions have brought about the most excellent results in many instances. I know that the contract system, with a salary supplemented by a bonus or participation in profits in special departments, has been used with great advantage to all concerned—by some of the most successful chemical companies in Continental Europe and in some of the more progressive American enterprises.

It has been objected that a contract of the kind merely binds the employer, who has tangible assets, while in most cases it would be difficult to enforce it against faithless employees. But even then a clear and well-defined contract will prevent many misunderstandings which will crop up in the course of time. It has been my experience that direct dishonesty and faithlessness are merely exceptions among chemists, whatever their other shortcomings may be.

The Chemist as a Restless Prospector.

We know where the work of the chemist begins. We can never tell where it ends, and through what unexpected ramifications it may lead. It is just this fact which adds some zest to the life of the struggling, hard-working chemist, and brings to his work frequently as much excitement as the best of sports. His hopes and disappointments can be compared to those of the restless prospector.

Pasteur, while he was Professor at the University of Lille, was consulted by a local alcohol distiller about some irregularities in the fermentation processes. Little did the great French chemist dream, when he tried to solve this purely industrial problem, that by doing so he was going to establish such an amount of new and unsuspected scientific facts destined to upset all formerly accepted notions, not merely on fermentation, but on life, disease, contagion, and epidemics; that he was about to revolutionise surgery, sanitation, and medicine, and create several new departments of medical science; that he was going to save millions of lives, reduce sorrow and misery. So little were the men of that period prepared for all these stupendous revelations that this great benefactor of the human race had to suffer most from the gibes and violent attacks of some of the best-known men of that very medical profession into which he was going to infuse new life by placing it on a true scientific basis. The history of the stubborn polemics and angry discussions at the French Academy show that, at that time at least, the imagination even of men of science could not expand to the point of perceiving that medicine and surgery were to be remodelled by the hands of a mere chemist.

EXTRACTION AND RECOVERY OF RADIUM, URANIUM, AND VANADIUM FROM CARNOTITE.*

By CHARLES L. PARSONS, R. B. MOORE, S. C. LIND,
and O. C. SCHAEFER.

THE work of the Bureau of Mines on radium began in the fall of 1912. A preliminary report published in the summer of 1913 outlined the conditions of mining and the wastes involved in the carnotite ore region of the West (*Bull.* 70, Prel. Rept., "Uranium, Radium, and Vanadium," by R. B. Moore and K. L. Kithil). As a result of this investigation, Dr. Howard A. Kelly, of Baltimore, and Dr. James Douglas, of New York City, were interested, and they incorporated the National Radium Institute. This institute leased certain carnotite claims in Long Park, Col., with the right to extract 1000 tons of carnotite ore therefrom. The National Radium Institute arranged with the Bureau of Mines for a co-operative investigation of the methods of extracting radium from this ore, and the saving of the wastes by the concentration of the low-grade ore formerly thrown on the dump.

Sufficient funds were furnished to be expended under the direction of the Director of the Bureau of Mines, and the first plant was built in the spring of 1914, beginning production on an experimental basis in June, 1914. The result of the preliminary investigation was so successful that the institute authorised the construction of a second and larger plant which began operations in February, 1915; the two plants have been run continuously since that time.

The object of the investigation was to procure an adequate supply of radium for the treatment of cancer in the two hospitals connected with the Radium Institute, and to develop methods of extraction whereby the miners might obtain a more adequate return for their ore, which, before this investigation began, had been sold largely to foreign manufacturers. Incidentally, methods have been developed for the preparation of sodium uranate, uranium oxide, and iron vanadate—by-products from the extraction of carnotite ore. Before the Bureau's operations began, several methods, the details of some of which have been kept secret, had been devised, for the extraction of radium from pitchblende and from carnotite. These involved (1) the use of an acid leach (2) the use of an alkaline leach followed by acid, and (3) fusing the ore with some material that would make extraction of the valuable contents possible. The acid leaches had been extensively used abroad, and had shown an extraction of not over 70 per cent, and probably little over 50 per cent of the radium content, owing to the fact that the ores contain sulphates, and any radium sulphate present was not removed under these conditions. The alkaline leach followed by an acid leach would probably remove more radium but involves such grave difficulties of filtration that it seemingly has not been put into commercial use. Fusing the ore with sodium sulphate was long employed on pitchblende (Haitinger, Luding, and Ulrich, *Ber. über die Bearbeitung der Pechblend-Rückstände* K. K. Akad. Wissenschaft., 1908, cxvii., 619), and has been used in Australia by Radcliffe in treating carnotite that is obtained at Olary, South Australia. This carnotite, being mixed with ilmenite, is very different from the American carnotite. Fusion with sodium carbonate has also been employed in this country on carnotite ores, but has the great disadvantage that it carries a large part if not all of the silica into solution. This adds greatly to the cost of operation and tends to give radium-barium sulphates of a rather high degree of impurity which require special treatment. From the best accounts available, it appears that this method

does not successfully extract more than 70 per cent of the radium present in the ore.

Method of Ore Treatment.

The method devised by the Bureau of Mines is based upon the fact that strong hot nitric or sulphuric acid dissolves radium-barium sulphates in considerable quantities, as well as the other soluble constituents of the ore. Hence the radium-barium sulphate left behind when dilute acids are used for leaching is obtained in solution and recovered. The use of strong hot nitric acid, although it presented many difficult problems of chemical engineering, was chosen because the radium-barium sulphate could be precipitated at once in a remarkably pure form, and the nitric acid could be largely recovered in the form of sodium nitrate and used again. Accordingly a nitric acid plant was built in connection with the radium plant, and has been regularly operating since February, 1915.

In the Bureau of Mines method the ore, pulverised to 20-mesh, is fed into an earthenware boiling kettle containing 38 per cent nitric acid. The nitric acid (121 lbs. HNO_3 diluted to 38 per cent) is brought nearly to boiling by means of steam passed through a glass-tube. When the boiling-point has been nearly reached the ore is added a shovelful at a time and the whole stirred, heating being continued. After the ore has all been added, heating is continued for fifteen minutes, when the mass is run on to an earthenware filter and the nitric acid separated from the ore by suction. The ore is re-treated with hot nitric acid of one-third the original strength, and is then washed with hot water. This treatment brings into solution nearly all of the uranium, about 50 per cent of the vanadium, and practically all of the radium present in the carnotite. The residue is discarded. The filtered solution is stirred, and sodium hydroxide is run in slowly with the object of reaching as nearly as possible the neutral point without forming a precipitate. If too much sodium hydroxide is added, both iron and vanadium are precipitated, discolouring the radium-barium sulphate. On the other hand, if not enough sodium hydroxide is added, the acid remains too strong and the solvent action of the nitric acid on the radium-barium sulphate is not sufficiently decreased. By a little practice the right point is easily obtained. Barium chloride is then added in the proportion of 2 lbs. of BaCl_2 to 1 ton of ore, and is thoroughly stirred in, and 15 lbs. of sulphuric acid to 1 ton of ore are then added. As the ore contains some barium it is necessary to add only a comparatively small amount of this material to accumulate the radium. The whole mass is vigorously stirred for one hour; the solution is then elevated to conical tanks where it is allowed to settle, usually for three to four days. The supernatant liquid is syphoned off for the recovery of uranium and vanadium, and the radium-barium sulphates are collected on an earthenware filter, washed, treated with dilute sodium hydroxide, and dried.

Radium Refining.

One of the most important features of the Bureau of Mines method is that the radium-barium sulphates first precipitated are of high grade, comparatively free from impurity, and are ready for immediate conversion into chlorides without further purification. The amount of radium in these sulphates has averaged about 1 mgrm. of radium element per kilogram. of material. It was early found in the work of the Bureau that the older methods of converting radium-barium sulphate into soluble form were unnecessarily tedious for the material produced. Accordingly other methods of reduction were tried, and it was finally determined that the best method to use is reduction with carbon in graphite crucibles. For this purpose the purest possible charcoal is used, about one-fifth the weight of the total sulphates being taken. The charcoal is mixed with the sulphates in a ball mill, and is then transferred to a No. 100 graphite crucible, and heated for seven to eight hours to a temperature around

* Authors' abstract from *Bull.* 104, U.S. Bureau of Mines. The bulletin contains complete detail descriptions of operations with full drawings both of floor plan and sections of the radium plant, as well as half-tones of plant and apparatus. From the *Journal of Industrial and Engineering Chemistry*, viii., No. 1.

800° C. Reduction takes place readily, the carbon monoxide burning out at the spout of the crucible. Three crucibles are heated in the same furnace. A reduction of over 90 per cent is usually obtained. The radium-barium sulphide is dissolved in pure hydrochloric acid, and the residue of unconverted sulphate is re-treated in like manner. The solution should, of course, be performed out of doors or under a hood with a good draft, especially as the hydrogen sulphide sometimes catches fire spontaneously; the danger is minimised if the residue is slowly added to the acid in an open vessel. In the re-treatment of the residues a third residue is also obtained. As there is a tendency to an accumulation of lead and other impurities in these residues, it is advisable to fuse the third residue with sodium carbonate rather than to attempt to reduce in the ordinary way with carbon. As the weight of the second residue is only 1 or 2 per cent of the original radium-barium sulphate treated, this special treatment is required only once or twice a year. The acid filtrate from the radium-barium sulphate is an almost saturated solution of radium-barium chloride and is ready for fractionation. Fractionation takes place much more rapidly in strong hydrochloric acid solution than it does if the solution is nearly neutral. However, the obtaining of containers that will withstand hot solutions of hydrochloric acid is difficult. Ware sufficiently resistant has been found in the silica-lined acid proof apparatus made by the Danto Rogeat Company, Lyons, France, and steam-jacketed kettles made of this ware have now been in use for over a year with almost no evidence of erosion.

For the first crystallisation, steam jacketed kettles of 250 litres capacity are preferable, although in a series of five the capacity of the last two need not exceed 200 litres. The evaporators are placed under hoods in order to remove acid fumes, and the evaporation is so conducted that the crystals move in one direction and the mother-liquors in the other, the crystals from a given evaporation being dissolved in the mother-liquors from the kettle second preceding. The crystallisation factor of hydrochloric acid solutions averages between 1.5 and 1.6; i.e., if 50 per cent of the barium chloride is removed there will be 50 per cent more radium in the crystals remaining, or if 50 per cent of the barium chloride is crystallised out there will be 50 per cent more radium in the crystals than in the liquor left behind. In a short time therefore the crystals in these larger kettles can be brought to a strength of 4 to 10 parts of radium per million; at this stage the crystals are taken from the plant to the laboratory for crystallisation in smaller apparatus of the same general type.

The salts of most metals, such as iron, aluminium, and vanadium, that may occur with the radium-barium solutions as impurities pass into the mother-liquors, and give no difficulty in the richer radium fractionations. Lead is, however, an exception and requires special treatment, although it might be expected that when the radium-barium sulphide is dissolved in hydrochloric acid, the copious evolution of hydrogen sulphide would remove the lead as lead sulphide. This does not occur owing to the high concentration of barium chloride, and the lead can be completely removed only after neutralisation with ammonia when the addition of ammonium sulphide causes it to be thrown down in an insoluble condition.

The crude radium-barium chloride containing 4 to 10 parts radium element per million is brought from the plant to the laboratory, where it is dissolved in water in large porcelain dishes, and hydrochloric acid is added. After the solution has stood over night it is filtered to remove the small part of lead that has been separated as chloride, and to remove whatever carbon and barium sulphate may have escaped previous filtration. After three or four re-crystallisations of the chloride, the chloride crystals are dissolved in water, the solution is made neutral with ammonia, and the lead is precipitated with ammonium sulphide. The solution is then filtered, and powdered ammonium carbonate is added until all of the barium has been precipitated as carbonate. The pre-

cipitate, of course, also contains radium as carbonate. It is washed and dissolved in chemically pure hydrobromic acid, after which crystallisation proceeds, an excess of hydrobromic acid also being desirable for the rapid separation of radium from barium. Usually ten or twelve fractionations are required in the form of bromides to bring the radium up to a strength of from 1 to 4 per cent radium bromide, the factor of concentration for each step in the hydrobromic acid solution being about 2 to 2.2. This makes rapid crystallisation possible. Every two or three days the strong crystals are placed aside until the end of the month, when they are mixed together in one lot and crystallised in hydrobromic acid solution to high concentration. Twelve to twenty crystallisations only are necessary to bring the major part of the radium to a concentration of 60 to 80 per cent radium bromide. One of the surprises of the radium work has been the ease with which separation of radium from barium is brought about. The crystallisation is rapid, and no difficulty whatever has been experienced in obtaining a high-grade material.

The bromide can be easily converted again into the chloride by one or two evaporations with hydrochloric acid, and in this form can be sealed in small glass tubes for transportation. The recovery of radium from carnotite shows so high an efficiency that over 90 per cent of the radium present in the ore may be recovered.

Separation and Purification of Uranium.

The acid solution from which the radium-barium sulphate has been precipitated is run directly from the settling tanks into large vats containing an excess of boiling sodium carbonate solution. Under these conditions the uranium and vanadium go into solution as sodium uranyl carbonate and sodium vanadate. For a solution from an ore containing 2.5 to 3 per cent uranium oxide, 250 lbs. of sodium carbonate in excess of that necessary to neutralise the acid originally used is required. This means about 650 lbs. sodium carbonate per ton of ore. It is important that the sodium carbonate solution be hot and be vigorously stirred, that the acid solution be added slowly, and that the boiling be continued for some time. Only in this way will the solution of uranium and vanadium obtained be anywhere near complete. Of course at the same time iron, aluminium, and calcium present in the solution are precipitated, and these are filtered off in filter presses, washed, and thrown away. The filtrate from the iron, aluminium, and calcium precipitate carrying uranium and vanadium is partly neutralised with nitric acid until a yellow precipitate just begins to form. At this point sodium hydroxide is added to the hot liquid until uranium is completely precipitated as sodium uranate. The sodium uranate at this point generally carries 7 to 9 per cent vanadic oxide, and must be precisely treated to remove the vanadium therefrom. This is best done by fusing the sodium uranate with salt in large wrought-iron or steel crucibles. When the salt is dissolved in water it carries the vanadium in solution as sodium vanadate, and leaves behind a practically pure sodium uranate.

Recovery of Vanadium.

The filtrate from the sodium uranate together with any sodium vanadate dissolved out of the sodium uranate by fusion with salt is brought to the boiling-point and neutralised with nitric acid, the boiling being continued long enough to eliminate carbon dioxide. At this point a solution of ferrous sulphate is run into the hot solution while under agitation by means of compressed air. As a rule about 75 lbs. of ferrous sulphate are required per ton of ore treated. The heating of the solution is stopped before the addition of the ferrous sulphate is complete, for if heating is continued longer a complete precipitation of the vanadium is not obtained. Iron vanadate obtained under these conditions usually contains 32 to 33 per cent V_2O_5 . The solution is slightly alkaline the percentage of V_2O_5 diminishes, while, on the other hand, if the solution is slightly acid when precipitation begins, a much

richer product can be obtained. This is accompanied, however, by a loss of vanadium, as some of it passes into the filtrate and causes difficulty in subsequent operations.

Nitrate Recovery.

After precipitation and filtration of the iron vanadate, the solution remaining contains chiefly sodium nitrate with small amounts of sodium chloride and sodium sulphate. It is evaporated to dryness, the sodium nitrate being crystallised out in crystallising pans, and used again for the production of nitric acid.

Recovery Averages.

Uranium.—In the extraction process previously described practically all of the uranium is dissolved in the nitric acid, only a small part (averaging 2.3 per cent) remaining in the insoluble residue because of incomplete washings. The loss of uranium in the iron calcium precipitate runs usually from 10 to 15 per cent of the material originally present in the ore. The recovery of uranium as sodium uranate has varied between 75 to 94 per cent of the uranium present in the ore, the average on the last ten carload lots treated being 84.4 per cent.

Vanadium.—The conditions making for the highest recovery of radium, which is the real value of the ore, do not generally coincide with the conditions necessary for the highest recovery of vanadium. It has accordingly been necessary to sacrifice the vanadium in order to get large recoveries of the more valuable element. Strong nitric acid tends to cause separation of vanadium from the solution, even after it has been dissolved, and this separated vanadium is filtered with difficulty and tends to decrease the radium extraction. More prolonged treatment with nitric acid would dissolve more vanadium, but this is not desirable, and it has been found best to use just as short a treatment with nitric acid as will ensure the complete extraction of the uranium. Fifteen minutes' heating in the extraction apparatus after complete addition of the ore is all that is necessary. Under these conditions, however, scarcely 50 per cent of the vanadium goes into the filtrate, and 15 to 20 per cent is lost in the iron calcium precipitate. Accordingly the total average recovery of vanadium, including that from the sodium uranate, has been a little less than 30 per cent of that present in the ore. The recovery of vanadium has barely covered the expense incident thereto.

Sodium Nitrate.—By using nitric acid for neutralisation throughout the process, a large proportion of the nitric acid used both for the solution of the original ore and for the neutralisation of the alkaline solutions is recovered in the form of sodium nitrate. During the months of May, June, and July, for which full figures are available, the average recovery was 87.5 per cent (minimum 84.87, and maximum 90.4). This high recovery has, of course, greatly decreased the expense of the nitric acid used in the operations as a nitric acid plant was built to work up the recovered nitrate. During May, June, and July, 1915, the expenditure for nitric acid was only 2.411 cents per pound of 100 per cent acid.

Radium.—When an element exists in an ore in the proportion of 1 part to 200,000,000, its extraction and recovery present difficulties not ordinarily encountered in metallurgy. A recovery of 60 to 70 per cent, or even 50 per cent might, under such conditions, appear to be satisfactory. A much larger recovery than 70 per cent is undoubtedly exceptional. The unusually high recovery of 90 per cent and over of the radium present gives the nitric acid method its real value.

Cost Data.

In figuring the total costs of the first 4258 mgrms. of radium element produced, the uranium and vanadium products may be either included or excluded. By subtracting the actual costs connected with the production of the uranium and vanadium compounds from the total costs, a close approximation of the cost of radium, provided the

uranium and vanadium were not recovered, will be obtained, but such a figure will not be exact, as under the changed conditions various factors would enter in, the effects of which can only be estimated. On this basis the average cost of 1 gram. of radium element, including the more expensive early treatment, is as follows:—

Cost of Radium Production to August 1, 1915.

Operating costs to August 1—

	Dols.	Dols.
Total expenditures	129,907.42	
Construction and equipment ..	52,453.60	
Cost of ore treated		77,453.82
Amortisation of plant and equipment at 20 per cent per annum		69,767.99
Cost of U.S. Bureau of Mines co-operation (plant department)		9,065.90
Cost of refining 2611.44 mgrms. radium element (estimated)		13,628.38
		5,353.00
		175,269.09
Less costs in connection with the production of the uranium and vanadium compounds		19,947.00
Total cost of 4258 mgrms. radium element		155,322.09

As already stated, refining losses have almost certainly been less than 2 per cent, and probably less than 1 per cent. In order, however, to be on the safe side, an allowance of 3 per cent is made for such losses; 4258 mgrms. less 3 per cent is 4131 mgrms., which represents the radium fully recovered as high-grade salts. The average cost of 1 gram. of radium element has therefore been 37,599 dols. It should be remembered that this cost included the proportionally much higher operating costs of the smaller experimental plant, and that the first 2 grms. of radium extracted cost considerably more per gram. than the last 3 grms.; also there have been extracted 31,650 lbs. of uranium oxide and 11,528 lbs. of vanadium oxide. This material has all been contracted for and in part delivered. The returns from its sale will considerably more than cover the cost of its production, and this profit, together with other credits, will ultimately lower by several thousand dollars the cost per gram. of radium.

As the price of ore is variable, the question will naturally arise as to the influence of the price of ore on the figures given above. A simple calculation will show at once that the cost of extracting radium, exclusive of the cost of the ore, has been 20.710 dols. per gram. The ore included in the figure of 69,767.99 dols. cited for the cost of ore used in the investigation herein outlined was partly purchased before the war and partly mined by the National Radium Institute at Long Park, Col. As 723.97 tons were used, the average cost was 96.36 dols. per ton. If the ore had cost 120 dols. per ton, the cost of radium would have been 41,742 dols. per gram., and for every additional amount of 20 dols. per ton above these figures the cost of radium would increase approximately 4000 dols. per gram.

HUNT FOR ACIDS.

EXPERIMENTS AT SOUTH WALES WORKS.

By HUGH H. BUSER.

It has been found that a solution of nitre cake can be used as a substitute for sulphuric acid or any mineral acid in chemical processes where acidity alone is required, and with this view interesting experiments are being made at the works of South Wales, more especially at those in the neighbourhood of Swansea.

Large quantities of sulphuric acid are used in tinplate works, but it is thought that nitre cake would not possess the acid strength to cleanse the tinplate of oxide. The preparation is stated to be suitable for the woollen industry and for calico bleaching, but it is not suitable when solutions stronger than 15 per cent are required. Thus it cannot be used in the dye-stuffs industry or in the manufacture of explosives.

It is possible that a further process may be evolved whereby the product would materially assist in tinplate manufacture. Up to ten years ago the general method of manufacture of sulphuric acid was the brimstone process, in combination with which nitrate of soda was used and nitre cake was the by-product of this process. Now sulphuric acid is produced largely from iron and copper pyrites and spent oxide.

A firm of Swansea producers are now erecting plant for the manufacture of sulphuric acid from waste gases at the local spelter works.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 3, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"An Orderly Dissimilarity in Inheritance from Different Parts of a Plant." By Prof. W. BATESON, F.R.S., and C. PELLEW.

"Observations on Coccozoic Flagellates, together with a Suggestion as to the Significance of the Kinetonucleus in the Binucleata." By H. M. WOODCOCK.

"Investigations Dealing with the Phenomena of Clot Formations. Part III. Further Investigations of the Cholate Gel." By S. B. SCHRYVER.

It is shown that there is a marked similarity between certain vital activities of cells and the behaviour of cholate gel.

1. The erosive action of certain organic substances on the cholate gel runs parallel with their narcotic and cytolytic actions.

2. Gel formation by calcium chloride is inhibited by sodium, magnesium, and other chlorides. The same substances can also cause gel erosion, but the erosive action can be antagonised by the addition of relatively small amounts of calcium salts.

3. To explain the parallelism between certain biological actions of organic substances and the antagonistic action of inorganic salts on the one hand and the action of these substances on the cholate gel on the other hand, it is suggested that the cell membrane or cytoplasm is constituted by a heterogeneous system of lipoids, proteins, &c., held together in a magma containing a gel forming substance with physical properties similar to those of the cholates. On such a hypothesis the biological action of certain substances can be explained in a manner more satisfactory than is possible by the assumption of the "lipoid" theory of Hans Meyer and Overton.

"Mechanism of Chemical Temperature Regulation." By J. M. O'CONNOR.

PHYSICAL SOCIETY.

Ordinary Meeting, January 28, 1916.

Prof. Sir J. J. THOMSON, O.M., F.R.S., President, in the Chair.

THE second Guthrie Lecture was delivered by Mr. W. B. HARDY, M.A., Sec. R.S., who took as his subject "Some Properties of Living Matter."

The lecture dealt with the physical aspect of some of the phenomena of living matter. At the outset some of the snares and pitfalls which beset the path of the physiologist in search of physical facts were indicated. One of these was the effect of instinct or intelligence in anticipating altered circumstances and in setting the appropriate physiological process in action even before the actual change in circumstance had taken place. For example, in some experiments to determine the time lag of increased respiration, it was found that the subject—a cyclist—always anticipated the application of the load and the acceleration of his breathing commenced *before* the actual increase in effort of which it should be the consequence. Then, again, many of the long-accepted theories of the structure of living organisms were ultimately found to be due wholly to the method of killing the organism and preparing it for examination. Exactly similar structures could be obtained in pieces of gelatin if treated in the same way.

Many phenomena were quoted to illustrate the close analogy of many of the functions of living matter to processes familiar to the physicist and physico-chemist. In some of these—for example, the digestive processes of certain organisms—the analogy was so complete that the whole process could be reproduced exactly with non-living material.

The principles underlying growth and development were outlined, and it was shown that growth depended on the presence in the food of *vitamines*. Thus, in the case of white mice fed on artificial milk, made by mixing together the purified constituents of ordinary milk but containing no *vitamines*, growth ceased altogether, while if 2 per cent of ordinary milk were added to the artificial milk the growth rapidly became normal. Another example of the influence of these *vitamines* was that in pure distilled water it was impossible to obtain a development of living organisms, but if the slightest trace of tap water were added—putting a stopper in the bottle which had previously been in a bottle of tap water was sufficient—the organisms would thrive quite normally. The fact that such small proportions of nutriment containing *vitamines* was sufficient suggested a parallel between their action and that of a few crystals thrown into a supersaturated solution of a salt in initiating a crystallisation of the whole.

A further example of the subtle influence of physical laws in physiological phenomena was contained in the explanation of the joining up of severed nerve processes. The directive action involved in this was stated to depend on extremely minute concentration gradients.

Many other interesting phenomena were described and explained.

SOCIETY OF CHEMICAL INDUSTRY (LONDON SECTION).

Ordinary Meeting, February 7, 1916.

Mr. ARTHUR R. LING in the Chair.

THE CHAIRMAN drew attention to exhibits of polarimeters and other optical instruments by two English firms, namely, Messrs. Adam Hilger, Ltd., and Messrs. Bellingham and Stanley.

The present highly developed state of the sugar industry, he said, was to be ascribed more to the control exercised in that industry by the polarimeter than to any other cause. The polarimeter was undoubtedly the most important instrument used in the sugar industry.

The particular form of instrument which the sugar manufacturer employed was the so-called quartz-compensating instrument. The analyser and polariser were in this case fixtures, and the rotation of the plane of polarised light by a sugar solution was determined in terms of thickness of quartz of opposite rotation. The fact that the different rays of the spectrum were rotated proportionately by sugar solutions and by quartz re-

spectively permitted the use with quartz-compensating instruments of ordinary lamp light instead of monochromatic light, which was employed by those instruments in which the measurements were made by rotating the analysing prism.

It was a remarkable fact that although there was such an extensive requirement for these quartz-compensating instruments in sugar-producing countries all over the world, up to the outbreak of war the supply had been exclusively from German and Austrian firms. He was glad to be able to welcome the instruments on the table, of British manufacture, which he had no doubt, in view of the high standing of the firms manufacturing them, would be found satisfactory. Unfortunately, it had not been possible for these firms to get the instruments ready in time for him to examine them before the meeting.

A fact to which he would like to draw attention was that quartz-compensating polarimeters ought not to be employed in the investigation of alkaloids, terpenes, and optically active substances other than sugars, since the rotatory dispersion of these differed from that of quartz.

The following papers were read:—

"Use of Enzymes and Special Yeast in Carbohydrate Analysis." By W. A. DAVIS.

The author showed that the ordinary analytical methods for the estimation of saccharose, raffinose, maltose, and starch frequently give quite unreliable results in the case of plant material, and he advocated the employment of special enzymes or yeasts as hydrolysing or fermenting agents respectively, which he found give reliable results.

In the estimation of saccharose by the double polarisation method two methods were suggested, namely, (1) inversion by digestion with a preparation of autolysed yeast at 38° C. for twenty-four hours, and (2) inversion with 10 per cent citric acid.

In the estimation of raffinose the presence of substances such as glutamic and aspartic acids, dextrose, and levulose, as well as pentoses, may impair the accuracy of the results. Raffinose is best estimated by fermenting solutions with pure cultures of top and bottom fermentation yeasts. Top yeasts hydrolyse the raffinose to melibiose and levulose, of which the latter only is fermented, whilst bottom yeasts hydrolyse the sugar to levulose, dextrose, and galactose, the latter remaining unfermented. The difference in the amount of hydrolysis effected by the enzymes prepared from top and bottom yeasts by autolysis can also be used to estimate raffinose, as recently suggested by Hudson and Harding.

The only reliable method of estimating maltose in the presence of other sugars is the use of the yeasts *S. marxianus*, *S. exigus*, and *S. anomalus*, which contain no maltase and therefore do not ferment maltose. Since pentoses are also unfermentable by the above yeasts, duplicate fermentations should be carried out with ordinary brewers' or distillers' yeast, the difference between the two sets of values giving the maltose. Starch is estimated by gelatinising and treating the paste with taka diastase, the enzyme of *Aspergillus oryzae*, which rapidly converts the starch into a mixture of maltose and dextrose, the proportions of which can easily be estimated from the cupric reducing and rotatory powers of the solution. This method is more accurate than those which depend on hydrolysis by acids or by malt diastase.

DISCUSSION.

Mr. JULIAN L. BAKER remarked that the length of time required for carrying out some of the methods might preclude their use for most commercial purposes. He defended the use of Lintner's method for the estimation of starch in materials when that carbohydrate was present in large quantities.

Prof. H. E. ARMSTRONG thought that Mr. Davis had developed a technique which enabled methods depending on the use of enzymes to be employed in the analysis of the carbohydrates.

Dr. L. T. THORNE thought that enzymic methods would

not entirely replace ordinary chemical methods in sugar analysis.

Mr. H. F. E. HULTON expressed surprise that in the author's experiments *Saccharomyces marxianus* was so slow in fermenting. He had found that a 5 per cent solution of citric acid hydrolysed maltose appreciably.

The CHAIRMAN, after complimenting Mr. Davis, said that large quantities of basic lead acetate had to be used for clarifying molasses, and for the analysis of the latter Ogilvie had developed a modification of the Clerget method depending upon the removal of the lead by sulphurous acid and the hydrolysis of the saccharose by invertase. He agreed with the author's remarks respecting the estimation of raffinose by the ordinary polarimetric method but he felt bound to defend the Ewer's methods of estimation of starch when certain corrections were applied.

Mr. DAVIS briefly replied.

"Acetic Anhydride." By J. T. HEWITT and C. H. LUMSDEN.

The authors reviewed the methods available for the preparation of acetic anhydride and similar compounds with the object of discovering the one most suitable for working on a manufacturing scale. The process, protected by Kessler (D.R.P. 132,605, of November 11, 1900), of heating together under a reflux condenser rather more than two molecular proportions of fused sodium acetate with one molecular proportion of sulphur chloride, S_2Cl_2 , and subsequently diminishing the pressure until the acetic anhydride distils, was found to work extremely well, and to give excellent yields of product, very little contaminated. Of the possible methods, those involving the use of sodium chlor. sulphate and sodium pyrosulphate were tried, but were not found to work using the apparatus available in the laboratory.

The authors concluded that the chlorides of sulphur and phosphorus are the most suitable reagents for use in the preparation of acetic anhydride, and that whether a sulphur or phosphorus chloride should be used is largely a matter of expense.

"Graphical Methods in Industrial Chemistry: (a) The Graphic Representation of Mixtures of Four Components; (b) A Simple Geometric Solution of an Engineering Problem Involving Three Variables." By E. HATSCHKE.

The first part of the paper described a simple method of representing tetrahedral co-ordinates in two dimensions, which is an adaptation of the general contour method to the tetrahedral diagram. The contours of a surface with equidistant planes parallel to one face of the tetrahedron are plotted in a series of triangular diagrams, the height of each triangle being equal to the height of the tetrahedron, less the distance of the contour plane from the base, so that all co-ordinates can be taken off the diagram true to scale. Problems amounting to the finding of tangent planes to a given surface, &c., can be solved in this contour diagram by very simple geometrical methods, without the necessity of making models.

The second part of the paper describes a simple geometrical solution of the following problem:—To find a graph for the time which a cylindrical tank takes to empty itself, both the height of liquid in it and the outlet area being variable. Although the equation connecting the three variables is cubic, a simple graph consisting entirely of straight lines obtained by geometrical constructions gives the complete solution.

Some remarks were made by Prof. BONNAU and Mr. HINCHLEY.

Phosphate Ores.—M. B. de Rollière, of Paris, announces the discovery of another new ore of high phosphorus content in the granites of France. It is a manganese phosphate extracted from a blackish brown rock in cleavable masses, and analyses as follows:—Phosphoric acid, 33 per cent; lime, 2.5 per cent; manganese oxide, 32.5 per cent; ferric oxide, 32 per cent.

NOTICES OF BOOKS.

Organic Chemistry. Volume I. Chemistry of the Aliphatic Series. By VICTOR VON RICHTER. Translated by PERCY E. SPIELMANN, Ph.D., B.Sc., F.I.C., A.R.C.Sc. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1915.

THIS book has been translated from the latest German edition, after the third American edition of Prof. Edgar Smith, and the German text has been very carefully and accurately followed, although a few corrections and minor alterations have been made. The original German references have been retained. As a work of reference, and for the general use of more advanced students of organic chemistry, the book is certainly without a rival in the English language. The subject matter is arranged in the most systematic and convenient manner, and the amount of detail compressed into it is surprising. Thus some account is given of the history of all the more important compounds, and many different methods of preparation are described in full, as well as the properties and reactions. After an introduction dealing admirably with the analysis of carbon compounds, their general physical properties, the action of heat, light, and electricity upon them, &c., the whole of the first volume is devoted to the aliphatic series, the aromatic and heterocyclic compounds being included in Volume II. There can be no doubt that the English will be as widely used and highly appreciated as the American edition, and the translator and publishers are to be congratulated upon having done a very useful piece of work for English chemists.

A Text-book of Paper-making. By C. F. CROSS and E. J. BEVAN. Fourth Edition. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1916.

THE latest edition of this text-book contains much additional matter, and has been partly re-written by the authors in collaboration with Mr. J. F. Briggs, whose long practical experience of paper-making has been of the utmost value. The book gives a full account of the chemical and physical properties of the raw materials used in paper-making, describes the methods employed in the manufacture, going into each step in detail, and also describes the testing of paper and its chemical analysis. It has been written in a thoroughly scientific spirit, and will be specially valued for the record it provides for the authors' pioneering work in the investigation of cellulose and the principles of paper-making.

Estudio de la Purificación de las Aguas por el Sulfato de Aluminio. ("Study of the Purification of Water by means of Aluminium Sulphate"). By Dr. ATILIO A. BADO and Dr. VICTOR J. BERNAOLA. Buenos Aires: Talleres Gráficos del Ministerio de Obras Públicas. 1915.

THE authors of this monograph have carried out a lengthy and comprehensive research on the rapid sedimentation of matter suspended in water, induced by the addition of aluminium sulphate. They have investigated the influence of various factors upon the action, finding, for example, that the quantity of sulphate necessary is a function of the alkalinity, and have studied the mechanism of the reaction. The data collected have been brought together in tables, and diagrams are given showing the variations in the organic matter, the alkalinity, and the matter in suspension of the water of the Rio de la Plata during the year 1914.

CORRESPONDENCE.

CLEANING IRON SHEETS.

To the Editor of the Chemical News.

SIR,—The present shortage (which is likely to become greater the longer the war continues) of sulphuric acid is seriously handicapping tinsplate and galvanising works in their pickling processes.

On page 58 of this month's *The Metal Industry* a reply on tinning states that iron surfaces can be cleaned by an alkali, such as caustic soda, &c.

If pickling (that is, the cleaning, or removing of the scale from steel sheets) by an alkali can be made a satisfactory alternative to sulphuric acid pickling, a great boon would at the present time be conferred on the industries I named at the commencement.

Any information that could be given me on this subject would be much esteemed.—I am, &c.,

MORGAN MORGAN.

MISCELLANEOUS.

New Reaction for Picric Acid and its Applications.
—J. Castels.—To detect picric acid an aqueous saturated solution of bromine is boiled with the solution, and after cooling by means of a current of water sulphuric ether is added. The liquid is well shaken, and the ether is decanted off, filtered, and divided into two parts. One is evaporated over warm water, and the light yellow residue is exposed to ammoniacal vapour when a more or less intense red coloration appears. The other portion is evaporated drop by drop on a piece of blotting-paper, which is then dried and divided into two. One of these fragments is exposed to ammoniacal vapours, when it turns red. A drop of potassium cyanide solution is added to the other and it is dried, when a zone of red coloration appears. This process can be used for the detection of picric acid in urine, by extracting with ether or chloroform, evaporating off the solvent, taking up the residue with water, and then treating as above. In the case of beer the liquid is evaporated and the residue is thoroughly shaken with alcohol. The alcohol is decanted off, the residue is extracted again, and the two alcoholic liquids are mixed, filtered, and distilled. The alcoholic residue of the distillation is treated with water, the alcohol is distilled off, and the residual aqueous liquid is strongly acidified with hydrochloric acid. It is then tested for picric acid as described above.—*Journal de Pharmacie et de Chemie*, 1916, xiii., No. 2.

MEETINGS FOR THE WEEK.

- MONDAY, 21st.—Royal Society of Arts, 4.30. (Fothergill Lecture). "National and Historic Buildings in the War Zone—their Beauty and their Ruin," by the Rev. George Herbert West, D.D.
- TUESDAY, 22nd.—Royal Institution, 5. "Nerve Tone and Posture," by Prof. C. S. Sherrington.
- WEDNESDAY, 23rd.—Royal Society of Arts, 4.30. "Experiences in Serbia," by Miss H. B. Hanson, M.D., &c.
- THURSDAY, 24th.—Royal Institution, 3. "Measurement of the Brightness of Stars—The Milky Way and Magellanic Clouds," by Sir Frank Watson Dyson.
- Royal Society, "Mathematical Contributions to the Theory of Evolution—XIX., Second Supplement to a Memoir on Skew Variation," by K. Pearson.
- "Relative Combining Volumes of Hydrogen and Oxygen," by F. P. Burt and E. C. Edgar.
- "Speed Effect and Recovery in Slow-speed Alternating Stress Tests," by W. Mason.
- FRIDAY, 25th.—Royal Institution, 5.30. "The Commerce of Thought," by Prof. Sir Arthur Quiller-Couch.
- SATURDAY, 26th.—Royal Institution, 3. "Eminent Generals of the last Great War—Sir John Moore," by Hon. J. W. Fortescue.

THE CHEMICAL NEWS.

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ON PROUT IN CONNECTION WITH AVOGADRO'S HYPOTHESIS.

By LEONARD DOBBIN, Ph.D.

P. J. HARTOG, the writer of the article on Dr. William Prout—the originator of the well-known "Prout's Hypothesis"—in the "Dictionary of National Biography" refers to Treatise VIII. of the "Bridgewater Treatises," entitled "Chemistry, Meteorology, and the Function of Digestion considered with reference to Natural Theology," of which Prout was the author, and states that "the book has little value from either a scientific or a theological point of view." While this may perhaps be accepted as on the whole a tolerably accurate estimate, there is one matter dealt with in the chemical part of the book which is of distinct historical interest, and regarding which all the more generally consulted works of reference on chemical history are silent. This is the particularly clear statement regarding the equality of the numbers of molecules contained in equal volumes of all gaseous bodies under the same pressure and temperature, and the consequences which follow from this hypothesis.

Avogadro, basing upon Gay-Lussac's Law of Gaseous Volumes, first definitely stated and supported this hypothesis in 1811, and drew conclusions from it as to the complex character of molecules of hydrogen, oxygen, chlorine, &c. After Avogadro (but prior to the publication of Prout's book in 1834) Ampère in 1814, Dumas in 1827-28, and Gaudin in 1833, also dealt with the matter; but Prout states that his views were adopted long before he was aware of the existence of the essays by Avogadro, Ampère, and Dumas, while it is unlikely that he had seen Gaudin's paper when this statement was written.

After treating (p. 60) of gases in respect to their diffusion, to their equal expansion by heat, to the inverse relation of their volumes to pressure, and to their similar capacity for heat, and adopting the hypothesis that "under the same pressure and temperature all bodies in a perfectly gaseous state contain equal numbers of self-repulsive molecules," Prout proceeds in a later section to consider consequences to which this hypothesis leads, and writes (pp. 122-3, 125):—

"Water has been shown to consist of one volume of oxygen gas and two volumes of hydrogen gas. . . . It has been also shown that the resulting water, if in the state of steam, occupies exactly the space of two volumes, so that one volume has disappeared. Now let us consider attentively what must have happened during these changes. One volume of oxygen gas has contributed to form two volumes of water, which two volumes of water, according to our hypothesis, must consist of twice the number of self-repulsive molecules contained in the one volume of oxygen, yet every one of these molecules must contain oxygen, because oxygen is an essential element of water; it follows therefore irresistibly that every self-repulsive molecule of oxygen has been divided into two, and consequently must have originally consisted of at least two elementary molecules, somehow or other associated, so as to have formed one self-repulsive molecule."

" . . . Muriatic acid gas is composed of one volume of chlorine and one volume of hydrogen, which unite without any condensation, and form two volumes of muriatic acid gas; now in this case it is evident that not only the self-repulsive molecule of hydrogen, but also that of the chlorine, must be double at least, like the molecule of oxygen above mentioned, and the same might be shown with regard to the other gaseous bodies."

It is to be noted that Avogadro's hypothesis was not accepted by chemists generally until some years after the appearance, in 1858, of Cannizzaro's "Sunto di un Corso di Filosofia Chimica," while Prout's clearly expressed views were published in 1834.

Chemists as a rule seem to have given little heed to this statement of Prout's views, and the only contemporary reference which the present writer has been able to find is some adverse criticism by Dr. W. C. Henry (*Phil. Mag.*, 1834 [3], v., 33), to which Prout replied (*Ibid.*, 132). His object in drawing attention to them now is to bespeak for them that mention in connection with the history of Avogadro's hypothesis which in his opinion they appear to merit, and which has hitherto been almost uniformly conspicuous by its absence. The only place where he has found Prout mentioned in this connection is in the brochure by Dr. A. N. Meldrum, entitled "Avogadro and Dalton: The Standing in Chemistry of their Hypotheses" (1904).

NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

Hedge-mustard (Alliaria officinalis).—This fine crucifer dwells only in certain dry shady waste or cultivated places. After emission from the seed the principal stem remains very short during the first year, and gradually becomes filled in its roots by starch and other reserves matters which the large radical leaves help to elaborate; in the second year vegetation is resumed in March, and the stem now develops very rapidly, issues leaves in all its length, followed soon by a terminal raceme of flowers, while the root reserves dissolve and are consumed. On May 24 the dried leaves yielded to boiling benzene 2.7 per cent of wax with much carotin and a little fat oil. The alcoholic extract contained little or no sugar, or resin, but had much of that remarkable flavone named saponarin, identified by giving a copious deep violet precipitate with iodine, by producing with alkalis and with Sn salt bright yellow solutions, and with FeCl₃ a deep brown; it yields no paracanthamin, and hence has no ortho group and no HO group adjacent to the chromophore; its decomposition product by acids has a clearly marked para group. Further treatment of the leaves showed the presence therein of very little sugar or mucilage, a little pentosan, no nitrate or reserve starch, but a distinct quantity of oxalate of calcium, although this salt does not appear as crystals in the leaf itself. The stem of this plant has no nitrate, tannin, or flavone, but has much sucrose and a little mucilage. The ash of the overground parts yielded 56.4 per cent soluble salts, 3.1 silica, 14.8 CaO, 3.5 MgO, 9.5 P₂O₅, 12.1 SO₃, and 6.3 Cl; there was only a little iron, manganese, or carbonates. The very long slender branched roots with a predominant wood tissue contained no starch or tannin at the end of May. The fruits (siliquæ) are very numerous, and the drain of nitrogen thereto is attested by the production of anthocyan in the autumn leaves, especially in their lower epidermises, the tint recalling that of the honeysuckle or of the guelder-rose. This plant does not vary under the influence of culture; for instance, it would not be affected by the application of nitrates because it has a powerful development of the root-system and copious water-conducting vessels; also the influence of other artificial manures upon it is forestalled, as it were, by its seeds developing naturally only in special habitats, and by its adaptation to a high intensity of light inducing a high limit for the temporary accumulation of carbohydrates, &c. Moreover, the fact that there is no nitrate in the leaves or stem of this plant, likewise the white flowers with their copious issue of fruits and seeds, clearly indicate that an amount of nitrogen and phosphorus sufficient for all requirements is readily procurable. The leaves when bruised yield a strong odour derived from a mixture of the sulphide and isosulphocyanate of allyl, the CS.NH₂ group

of the protein molecule probably being concerned in the deassimilation. The fact that the Cruciferae generally are injured by NaCl, and that therefore they may absorb heavy doses of sulphates, does not seem to be a paramount factor here, inasmuch as in the monocotyledon genus *Allium* glucosides occur which yield allyl derivatives of a pungent garlic odour, while the ash of the leaves of *A. ursinum* contains 21.5 per cent Cl and only 6 SO₃, and that of *A. porrum* 6.6 and 4.1 respectively. The cleavage of the complex glucoside is supposed to be effected by a ferment myrosin which is formed in the vacuoles of special resting cells in process of disorganisation, which have a very granular protoplasm and a quantity of amorphous proteid matter, but have no starch, fat, or aleurone; water is not necessary for this decomposition. It is obvious, however, that there is a good deal of postulation about this account of the phenomenon. It is quite possible that the action of bruising the leaves, &c., merely increases the pressure of the water contained in some of the cells, with the result that the volatile oil already elaborated is simply set free and there is no glucosidal combination.

Tufted Vetch (*Vicia cracca*).—This is a member of an order (Leguminosae) which represents the highest embryological development as regards structure and nutrition, and with powers of variation and adaptation to environment second to none, &c. It is a characteristic plant of sandy soil, whereas most other legumes require lime and mineral manures; it is found in hedges, thickets, alluvial fields, &c., wherein it establishes a rhizome fixed by numerous adventive roots and forming a veritable network of ramifications. The chemistry of this plant is, apart from its seeds, rather tame. On July 18 the dried overground parts yielded 1.7 per cent of carotin and wax, with little or no glyceride. The alcoholic extract contained a mere trace of a flavone like luteolin, also some alkaloidal matter, a resin, and a little sucrose and citric acid; there was no tannin, glucose, or amaroid. The remaining constituents consisted of much pectosic mucilage, a little pentosan, and oxalate with citrate of calcium; there was no extractible proteid or starch. The ash amounted to 6.8 per cent, and yielded 19 per cent soluble salts, 2.2 silica, 40.6 CaO, 3.8 MgO, 4 P₂O₅, 2.5 SO₃, and 2.2 Cl; there was a little iron, manganese, and soluble carbonate. There was about 27 per cent albumenoids in the dry material, the crude fibre amounting to only about 20 per cent. There was no detectable nitrate in this or other species of vetch examined (distinction from melilot, French bean, clover). The flowers afford a fine example of a pseudo-blue, their colour being frequently called blue, but it is really a vivid violet or a warm bluish purple, which is greatly helped out by the height of the plant, the smallness of the leaf area, and the long peduncles. The seeds contain constituents similar to those of the common vetch (*V. sativa*), viz., fatty matters (including lecithin, nuclein, glycerides, with traces of phytosterol), about 30 per cent starch, some citric acid, sucrose, and much insoluble carbohydrates (galactan, pentosan, some pectosic mucilage, &c.), but no tannin, alkaloid, vicianine, or oxalate; also they have about 20 per cent nitrogenous matters consisting of albumenoids and globulins, and the germinability of the seeds depends on the solubility of the latter. The seeds have no endosperm, their cotyledons are cellulosic, and bear aleurone and starch as reserves. It has been stated that a distinct relationship exists between the distribution of Azotobacter and the Leguminosae; the bacterium has most intense respiration, can fix 17 mgrms. N per gm., and produces no acids, &c. Also it is known that Leguminosae have acquired contrivances in order to increase transpiration, are made independent of the nitrogenous matters of the soil, and have a very deep root system and strong root acidity, &c. They depend only slightly on mycorrhiza, form starch very rapidly in their leaves, and have no water-excreting organs. Some of them, however, as the yellow lupine and the tufted vetch, eschew lime soils, but their ash contains a great amount

of lime in soils poor in this earthy carbonate, the reason assigned being that it is imperative for them to live in acid soils, otherwise they are unable to absorb sufficient phosphoric acid for the maintenance of their vitality; i.e., for the circulation of their nitrogen. The main fact, however, is, as we have seen, the abundance of acid matters showing the tendency of the protoplasm on deassimilation to detach its carbon and hydrogen in the state of organic acid, and not so much as free CO₂ and H₂O or as tannin. It has been asserted that the lime is required for the nitrifying germs when the soil is poor in nitrates; but the largest amount of nitrate that I have ever found was in the overground parts of the garden cress, the ash of which yielded only 9.6 per cent CaO.

Bogbean (*Menyanthes trifoliata*).—This beautiful member of the order Gentianaceae grows in peat bogs in the interior; i.e., in soils where certain acids and ulmin are produced and no humus, their nitrogen being in the form of a kind of protein with very little amino-acid or ammonia. The analysis is of great importance, inasmuch as it represents almost the only available plant of the order which can be said to contain in this country a full development of chemical constituents. On June 14 the dried leaves yielded 1.5 per cent white wax with much carotin and some phytosterol. The alcoholic and aqueous extracts contained a little flavone which was not quercitrin, also about 3 per cent caffetannin with very clear and decisive reactions, and a carbohydrate which in acid solutions gave strong reactions of sucrose (is probably inulin, and not gentianose); there was a small quantity of an amaroid named menyanthin, which is amorphous, yields 28 per cent glucose on hydrolysis, and dissolves in sulphuric acid with brown to fine red colorations. There was only a little mucilage and some reserve starch, and but mere traces of nitrate or oxalate. A purified aqueous extract of the leaves was evaporated and potass fused whereby protocathechuic acid was obtained, but no trace of phloroglucol. The ash of the dried leaves amounted to 8.6 per cent, and yielded 38.9 per cent soluble salts, 4.1 silica, 20.2 CaO, 4.5 MgO, 7.1 P₂O₅, 6.8 SO₃, and a trace of Cl; there was much soluble carbonate, and about 5 per cent oxides of Fe and Mn. There is evidently much organic acid produced by this plant, and owing to its early flowering, the proteids (about 15.7 per cent in June) of the leaves show little decline till later on. The rhizome is a remarkable organ; it is formed of rings whose central portion encloses isolated bundles quite like that of aquatic monocotyledons, its cortex and pith are formed of bead-like wreaths of cells surrounding inter-communicating air-passages, and its branched side-roots are provided with hairs and have no mycorrhiza. It contains over 1 per cent of caffetannin, much inulin, pectosic mucilage, and pentosan, some amaroid and nitrate, but no starch, alkaloid, or oxalate. It is obviously difficult in this case to assign the origin of the nitrate here to any other source than that of the physiological activity of the plant itself. The flowers are pink, but the only other species of *Menyanthes* has bluish flowers, the reason being no doubt that it inhabits drier and less acid soils where organic nitrogen is not so available. The bogbean is related to the glorious gentians of the Alps which in their thousands star the ground with sapphire. Their liber and peripheral pith bear masses of sieve-tubes which are the carriers of proteids, but the Alpine soil is poor in nitrogen, only to be obtained (so it is said) from atmospheric ammonia. In all cases the gentian pollen is large, and the ovules and seeds extremely numerous. Their leaves are mostly linear or lanceolate and the corolla comparatively large; hence there is a severe drain on its proteid (amido groups), the protoplasm deassimilating under their privation yields an original blue pigment quite in harmony with the mildly reacting caffetannin, which is the tannin native and natural to its constitution.

On Poppies.—As most of these remarkable plants seem to have been chemically ignored or neglected, I have thought it worth while presenting the results of my own

examination of some of them. Only the aqueous extracts can be dealt with on this occasion. The leaves and part of the stem of the garden Shirley poppy (*Papaver rhæas*) were cut up and boiled in water, filtered, &c., and by means of the usual treatment the solution was found to contain considerable nitrate, mucilage, and sucrose, a little caffetannin and alkaloid, but no flavone; the stem had more tannin than the leaves. The leaves of *P. orientale* contained alkaloid, nitrate, and much sucrose, also much flavone, but very little caffetannin, perhaps none; this negative result being evidently due to the copious development in size and weight of the foliage; the flavone was not quercitrin. The magnificent opium poppy (*P. somniferum*) leaves contained very much nitrate and limy mucilage, a little sucrose, and some free glucose, also a considerable amount of a flavone not related to quercetin, and about 2 per cent caffetannin; this plant produces oblong and comparatively small and few leaves, and hence here the reactions of tannin are much more pronounced than in the two other species aforesaid. The chemistry of the leaves of the Welsh poppy (*Meconopsis cambrica*) has been already treated by me in CHEMICAL NEWS (1914, cix., 146), whence it will be seen that it is similar to that of the true poppies; the yellow petals of this plant contain no flavone or anthocyan; but their alcoholic extract gives decisive reactions of the alkaloid berberine, and no doubt is to this constituent that the yellow coloration of the flowers of this and of some other poppies is due. On the other hand, the yellow and orange corolla of the Californian poppy (*Eschscholtzia*) owes its bright pigment to carotin, and it has only a trace of alkaloid. The preceding analyses are, perhaps, more important than what would have been foreseen. Systematically, poppies have been approached to water-lilies, but they have more affinity to crowfoots, which, however, have watery and not milky juices. According to Faltis the alkaloids of poppies, fumitorys, barberry, moon-seeds, &c., are all derived from one uniform stock-substance. All these and crucifers are inter-related, and all produce caffetannin, and are capable of exhibiting true blue flowers.

Some Winter Phenomena.—Even in the dead waste and middle of winter the labours and researches of the chemist of plants need not cease. Not to mention the examination of the wood and bark of various trees with reference to their tenure of starch. &c., interesting enquiries may be conducted respecting the chemical condition of various perennial roots, tubers, &c., which remain alive during the dead season. Carefully avoiding any field or homestead where sheep or other cattle had browsed or haunted, a small quantity of the roots of grasses was dug up, and as soon as possible immersed in boiling water, left over night, boiled up again, filtered, cooled, and treated with basic acetate of lead, &c. The solution in all cases was very gummy, which made the filtration rather tedious, and the lead precipitate was rather scanty. However, in all cases two constituents were found, viz., nitrate and a carbohydrate yielding levulose, and whether the roots were fibrous or creeping, short and voluminous, or long and fine, the results were invariably similar. A clump of moss growing isolated on a horizontal top stone of a dry wall also contained the same kind of gummy matter, had considerable nitrate and pentosan, but was lacking in starch and sucrose. Another clump of moss perched on the stump of a decayed ash-tree at about 4 feet from the ground contained the same constituents, albeit in more moderate quantity; sucrose was, however, detected in this case. The question arises as to how and where do these mid-winter plants obtain the nitrate which they contain? A piece of bogbean rhizome that had been severed and tossed by the winter wind upon the shore of the tarn where it grew was found to contain a good deal of nitrate. This rhizome is highly porous and pervious to water, yet, nevertheless, the soluble nitrate had been retained therein. If in any of the aforesaid cases the nitrate had been absorbed from the soil is it likely, as Demoussy thinks, that "the nitrates accumulate

in the living organs where they become insoluble, the protoplasm retaining them with an energy comparable to chemical affinity, but they quit it at the moment of death?" Grasses, says Deherain, "store up nitrates during winter for future use"; but I am inclined to agree with Berthelot that in the above cases most of the nitrate has been formed by the physiological activity of the plant itself.

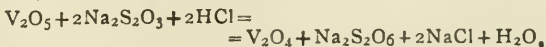
Patterdale, Westmorland.

THE ESTIMATION OF PENTAVALENT VANADIUM BY MEANS OF SODIUM THIOSULPHATE.

By G. O. OBERHELMAN.

As is well known, standardised sodium thiosulphate in excess may be employed under certain definite conditions as a reducer of ferric chloride, the amount of the thiosulphate which disappears by transformation to tetrathionate (determined by the idiometric determination of the excess) serving as the measure of the ferric salt reduced. In this process, originally proposed by Scherer (*G. Anzeig. k. Bayrisch. Acad.*, August 31, 1859) and studied by many investigators, there are three sources of error which may appear, according to conditions—viz., incompleteness in the reduction of the ferric salt, decomposition of the thiosulphate by the action of free acid, and progressive oxidation by the action of the air. Norton (*Am. Journ. Sci.*, 1899, [4], viii., 25) has shown that these sources of error may be made to disappear by the use of a sufficient excess of sodium thiosulphate, by regulation of the time of action, and by attention to the concentrations of free acid, thiosulphate, and the ferric salt. According to Norton's procedure the volume of the solution should be at least 400 cc. for each 0.1 grm. of iron oxide present, the quantity of free hydrochloric oxide present should not exceed 1 cc. of the strongest aqueous acid to each 400 cc. of solution, the excess of N/10 thiosulphate should amount to at least 15 cc., and this excess should be determined by titration with N/10 iodine as soon as the colour brought out in the solution before reduction, due to the addition of a drop of potassium sulphocyanide solution, has been discharged. Oudermanns (*Zeit. Anal. Chem.*, ix., 362) has recommended the introduction of cupric sulphate as a catalyser to hasten the process of reduction, but Norton found this procedure unnecessary.

This paper is the account of a successful attempt to adapt a similar process of reduction by sodium thiosulphate to the determination of vanadic acid (in the course of work the account of which will be published later) under conditions in which the ordinary modes of determination are impossible or inconvenient. It has been found that the action of reduction may be made to proceed regularly in the sense of the expression—



The amount of vanadium present may be measured by the difference between the amount of standard thiosulphate introduced and the amount of that reagent remaining, as determined by titration with standard iodine, but in this case, unlike that of the reduction of the ferric salt, the presence of a catalyser is necessary to bring about the reduction of the vanadic acid, and the concentration of the free hydrochloric must be slightly larger than that indicated by Norton as applicable in the reduction of the ferric salt. When considerably larger amounts of hydrochloric acid are present the thiosulphate is decomposed with the liberation of sulphur dioxide, which of course entirely vitiates the process.

On the introduction of thiosulphate into a solution of ammonium vanadate containing a little copper sulphate and slightly acidified the golden yellow changes to green,

and finally to a pure blue, which indicates reduction of the vanadium to the tetravalent state. With iron it is necessary to introduce a little sulphocyanide as an indicator of complete reduction; with vanadium no outside indicator is necessary. When the solution has become a pure blue it is only necessary to add starch, with enough potassium iodide (0.1 to every 100 cc. of solution) to bring out a sufficiently delicate end-point (Hale, *Am. Chem. Jour.*, xxviii., 938) before proceeding with the titration by iodine.

Certain experiments showed plainly that with a certain amount of copper sulphate and hydrochloric acid present the rapidity of reduction depends largely upon the concentration of the acid. It was found that to bring about complete reduction within a reasonable time as much as 1.5 cc. of the (32 per cent) acid should be present in every 400 cc. of solution, and that this concentration of acid does not cause appreciably, at ordinary temperature and during the period of reduction, a secondary decomposition of sodium thiosulphate (resulting in the liberation of sulphur dioxide), provided the excess of this reagent does not exceed the equivalent of $7\frac{1}{2}$ cc. of the N/10 solution in the 400 cc. (compare Norton, *Am. Journ. Sci.*, 1899, [4], vii., 287). In the quantitative tests of the process detailed below the concentrations of acid and thiosulphate were kept within these safe limits. Moreover, since copper sulphate and potassium iodide react at sufficient concentrations with the liberation of iodine according to the expression

$2\text{CuSO}_4 + 4\text{KI} \rightleftharpoons \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$, it is plain that in the reduction of vanadic acid by the thiosulphate the amount of copper sulphate used as a catalyser should be kept if possible well within the maximum, which may be present without setting up in appreciable degree the reactions by which iodine is set free. Table I. contained the results of experiments made to discover the amount of copper sulphate which may be present in a solution of 400 cc. or a little more in the presence of 1.5 cc. of 32 per cent hydrochloric acid and potassium iodide in varying amounts. The starch reaction was observed after a little more than the lapse of time which would occur in the titration of the excess of thiosulphate by iodine in the vanadic acid determination.

TABLE I.—The Action of Copper Sulphate upon Potassium Iodide with Liberation of Iodine.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Grm.	HCl (32 p.c.) Cc.	KI Grm.	Volume Cc.	Starch reaction.
0.0100	1.5	0.4	410	None
0.0100	"	0.8	420	"
0.0100	"	1.2	430	"
0.0200	"	1.2	440	"
0.0300	"	1.2	450	"
0.0300	"	1.6	460	"
0.0300	"	2.0	400	Blue
0.0300	"	2.4	400	"
0.0200	"	2.4	400	None
0.0100	"	2.4	400	"

From the results given in Table I. it would appear that in presence of 1.5 cc. of (32 per cent) hydrochloric acid in the water solution of approximately 400 cc. there is no appreciable liberation of iodine when so much as 30 mgrms. of the copper sulphate and 1.5 gm. of potassium iodide are present. When, however, even smaller amounts of the copper salt and iodide are present during the reduction of vanadic acid by the thiosulphate taken in slight excess (2 to 5 cc.) an appreciable over-use of thiosulphate appears.

In studying the conditions for the quantitative estimation of vanadium the solutions used were made from ammonium vanadate and standardised by means of the Holverscheit method ("Inaug. Diss.," Berlin, 1890), according to which the vanadate is treated with potassium bromide and hydrochloric acid and the liberated bromine determined by absorption in a solution of potassium iodide and titration

of the liberated iodine. The thiosulphate solution, approximately N/10, was standardised against N/10 arsenite made from twice sublimed arsenic trioxide. The amounts of copper sulphate were restricted to a maximum of 10 mgrms. in a volume of 400 cc. and the iodide to about 0.1 gm. for every 100 cc. of solution. Qualitative experiments showed that the reduction of the vanadic acid might be considerably accelerated by the presence of an excess of the comparatively insoluble cuprous iodide, used as the catalyser in place of copper sulphate, but the quantitative tests indicate that the reduction is not complete and that the addition of cuprous iodide to solution charged with a sufficient amount of the copper sulphate is without apparent effect. The experiments of Table II. show the effects due to variation in the amount of the catalyser under conditions otherwise similar.

TABLE II.—Reduction in Presence of an Excess of Thiosulphate amounting to 2 to 5 cc. of the N/10 Solution in a Volume of 400 cc.

V_2O_5 taken. Grm.	V_2O_5 found. Grm.	HCl (32 p.c.) Cc.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Mgms.	KI. Grm.	Volume. Cc.
0.1583	0.1560	1.5	—*	0.45	400
0.1583	0.1555	1.5	—*	0.45	400
0.1955	0.1942	1.5	3*	0.45	400
0.1955	0.1950	1.5	5*	0.45	400
0.1955	0.1952	1.5	7*	0.45	400
0.1955	0.1957	1.5	8*	0.45	400
0.1955	0.1958	1.5	8*	0.45	400
0.0977	0.0985	1.5	8*	0.45	400
0.0977	0.0985	1.5	8*	0.45	400
0.0977	0.0983	1.5	8*	0.45	400
0.1955	0.1966	1.5	10*	0.45	400
0.1955	0.1957	1.5	5	0.4+	400
0.1955	0.1957	1.5	5	0.4+	400
0.1955	0.1957	1.5	5	0.4+	400
0.1955	0.1955	1.5	5	0.4+	400
0.0977	0.0980	1.5	5	0.4+	400
0.0977	0.0979	1.5	5	0.4+	400
0.0977	0.0980	1.5	5	0.4+	400

* Cuprous iodide also present in suspension.

The results obtained are below the theory when cuprous iodide was the only catalyser, fairly good when cupric sulphate was also present in amounts varying from 5 to 10 mgrms., and very close to theory when cupric sulphate present to the amount of 5 mgrms. was the only catalyser. The progress of the reduction was, however, rather slow, and the expedient of increasing the excess of thiosulphate in order to accelerate the action was tried. At a volume of 400 cc., however, 1.5 cc. of the 32 per cent hydrochloric acid will liberate from the equivalent of 15 cc. of N/10 thiosulphate enough sulphur dioxide to be recognised by the odour. In the following experiments, therefore, the total volume of the solution was doubled, with corresponding increase in the concentration of acid and iodide, while the excess of N/10 thiosulphate was placed at 15 cc.

TABLE III.—Reduction in Presence of an Excess of Thiosulphate amounting to 15 cc. of the N/10 Solution in a Volume of 800 cc.

V_2O_5 taken. Grm.	V_2O_5 found. Grm.	HCl (32 p.c.) Cc.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Mgms.	Excess of N/10 $\text{Na}_2\text{S}_2\text{O}_3$. Cc.	KI (gm.) present.	Vol. Cc.
0.0967	0.0965	3	10	15	0.8	800
0.0967	0.0967	3	10	15	0.8	800
0.1935	0.1932	3	10	15	0.8	800
0.1935	0.1937	3	10	15	0.8	800
0.3870	0.3866	3	10	15	0.8	800
0.3870	0.3876	3	10	15	0.8	800

In these experiments, obviously excellent, the rapidity of the process was much increased by the limited increase in the concentration of the thiosulphate. The results

seem to justify the conclusion that if the conditions are carefully controlled pentavalent vanadium may be rapidly and accurately estimated by direct reduction with sodium thiosulphate and titration of the excess.

According to the procedure recommended the vanadate solution is brought to a volume of 800 cc. or 400 cc., 10 mgrms. or 5 mgrms. respectively of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and 3 cc or 1.5 cc. respectively of hydrochloric acid (32 per cent) are added; N/10 thiosulphate is slowly run in, with constant stirring, until an excess of 15 cc. or 7.5 cc. respectively is present; the solution is allowed to stand until its colour has become a pure sky blue, potassium iodide to bring the amount up to 0.1 gm. for each 100 cc. of solution is added, and the excess of thiosulphate is titrated with N/10 iodine in the presence of the starch indicator. The vanadium blue interferes but slightly with starch blue end-point.

When the amount of vanadate to be determined is not approximately known, a preliminary determination, in which the copper sulphate is used to the amount of 20 mgrms., will quickly give the information required for the proper adjustment of the thiosulphate in an exact analysis to follow.—*American Journal of Science*, xxxix., p. 530.

POSSIBLE SOURCES OF POTASH IN AMERICA.

By FRANK K. CAMERON, Ph.D.

Introduction.

THE absolute value of the potash market in the United States under normal conditions is relatively small when compared with that of many other products, being in the neighbourhood of 12,000,000 dols. Its importance is very great, nevertheless, for potassium salts are almost a necessity in the production of some of our crops, and are desirable in the production of practically all of them. There are other than agricultural uses where the consumption is much smaller but where the necessity is even more pronounced, as in the production of certain types of soap and certain kinds of glass. Normally this country obtains about a million dollars' worth of potassium nitrate, nearly all of which comes originally from India, although not always directly. Practically all of this potassium nitrate is used in making fireworks and certain types of powder.

As matters stood before the present European conflict the consumption of potassium salts for military explosives was insignificant, but it is one of the surprises of the war, even to chemists who are not also experts in military matters, that the conflict has brought about such a tremendous demand for types of munitions in which potassium seems to be a necessary constituent, for which there appears to be no satisfactory substitute. Aside from potassium nitrate, as all the world now knows, the whole world's supply of potassium salts came from Germany, from the famous Stassfurt region, and from the less well known Alsatian deposits, of rapidly increasing commercial importance.

The controversies of the year 1909-10 between American importers, the German Kali Syndicate (a selling agency under Imperial supervision), and certain independent producers in Germany, led to diplomatic exchanges between the Government of the United States and the German Imperial Government, which served at least one good purpose, in focussing attention in this country upon the desirability of developing native sources, a desirability confirmed and made more insistent by the unhappy predicament now confronting us. Governmental investigations have been actively in progress since, and private initiative has been greatly stimulated. As a result it has been shown that there are a large number of possible sources of soluble potash salts within the United States, some of which are quite valuable possibly to particular owners, and three and possibly four are potentially possible sources of large commercial importance. At the

present writing there is a very small amount of potash salts on hand. The munition manufacturers have been and are still buying eagerly. They prefer the chloride to the sulphate, which is interesting for at least two reasons—it gives a clue to what they are doing with the potash, and it has brought the price of potash, unit for unit, to a higher price in the chloride, though normally the reverse is the case, the sulphate being more highly valued for fertilisers and the chemical industries generally.

No one seems to have any idea, even approximately, as to the aggregate amount of potash salts now in the hands of fertiliser manufacturers and brokers, but it is very clear that the rapidly diminishing imports have about reached the vanishing point, although the world has been scoured for existing stocks, and purchasers for the United States have been as far as Batavia, Borneo. From very recent events it is rather convincingly evident that the embargo on supplies from Germany is not to be lifted until the end of the war. From this point about everything one can say about potash salts is highly speculative. It seems reasonable to expect that prices will be much higher after the war than before unless workable sources are developed outside of Germany, for potash salts form one of that country's resources that can and probably will be made to shoulder a very large part of the war's expenses. For this reason the ultimate ownership of the Alsatian deposits is of particular interest to the world at large. The Galician and Spanish deposits, as well as those reported from Peru, are possibly of importance, but the information concerning them that is now available offers very slim hopes.

In so far as the technical features are concerned it has been demonstrated that the United States can produce far more than its own needs in potash salts. Undoubtedly the technology is susceptible of improvement, and of possibly very great improvement, but the potash can be produced, and the real difficulties in the way of a realisation of potash production in the United States are purely commercial and not physical.

Felspar.

Of the several possible sources attention naturally is commanded first by the potassium silicates, such as orthoclase, muscovite, sericite, or leucite, of which large deposits exist in many regions of the country carrying 10 per cent or more of potash (K_2O). There are probably a hundred patented processes for the extraction of potash from such materials, all of which processes fall into two classes. In the first class the spar or other silicate is mixed with coal or coke, lime, calcium chloride, sodium chloride, nitre coke, or some combination of these substances, and heated to form a sinter, from which the potash salt is leached. To evaporate the leachings another supply of heat is required, and the final product is never the pure potassium salt but a mixture with other less desirable substances. To recover all the potassium salt in a pure state by crystallisation methods alone is impossible, and to recover it by further chemical manipulations is prohibited by the cost. To meet these objections the second class of processes has been devised, in which the original mix is heated to melting, and thus the potassium is volatilised either as the oxide or as the chloride. Some of the proposed methods have now been tested on a sufficiently large scale to demonstrate their practicability so far as the physical factors are concerned, and one of them has actually produced a few tons of potassium chloride and oxide.

It is claimed by promoters of these processes that there are known large deposits of spar or other potash silicates which can be worked on the steam-shovel plan, and which will yield "run of the mine" material containing 10 per cent or more potash at a low working cost. Usually these costs of producing the raw material have been stated to be in the neighbourhood of 1.50 dols. per ton. These claims may in some cases be valid, but it is difficult to find a disinterested authority who thinks that there is a deposit from

which 10 per cent potash spar can be obtained on a commercial scale without hand cobbing. This would make the cost of production prohibitive, and apparently no disinterested investigator considers it practicable to work a product that approximates 10 per cent or more potash. But in all fairness to the promoters of potash from felspar it should be said that the case is not a proved one either for or against them, in this regard at least.

Again every disinterested investigator seems to be convinced that potash from felspar or other silicate mineral is commercially impossible under normal conditions of the market unless the by-product or residue is saleable. So far there seems to be but one practical suggestion—to utilise the residue in making cement. Apparently very good cements can thus be prepared, in some cases cements of very desirable special qualifications. But the cement industry is a large one, worth many times the potash industry. It has grown very rapidly and is now standardised. Practically all cement is now sold under standard specifications, which are not met by the felspar cements without reference to their intrinsic merits. The cement manufacturers, therefore, are not and cannot be expected to be willing to remodel their plants, re-train their operatives, secure (if that be possible) a source of spar, and re-educate the buying public, thus risking the larger and sure business on the chance only of securing a much smaller one.

Certainly one, and if newspaper reports can be trusted several, cement plants are now actually recovering and marketing flue dust containing a relatively high percentage of water-soluble potash. At the abnormally high prices which the product now commands such flue dust can profitably be collected, and prove a godsend to certain consumers of potash salts, as, for instance, the manufacturers of liquid soaps. It is very doubtful if these dusts could maintain a market under normal trade conditions.

Desert Basins.

All desert basins, speaking generally, contain considerable stores of water-soluble potassium salts, but usually so mixed with insoluble fill derived from the rim rock as to be quite impossible as commercial sources. A very large number of the desert basins have now been explored more or less thoroughly, and with one exception it can now be said that the chance of finding a segregated deposit of potassium salts capable of being exploited commercially is a "miner's chance" only, and a poor one at that. Searle's Lake, in San Bernardino County, California, is in the ordinary weathers of the desert—a mud flat, but below the surface the solid material is mixed with a brine carrying 5 or 6 per cent potash, in the form of the chloride mainly. But there are large percentages of other soluble substances present—sulphates, carbonates, and borates, as well as chlorides of sodium and magnesium, as well as of potassium. It is impossible by crystallisation methods alone to recover all the potassium from such a brine in anything approximating a pure salt or a mixture of potassium salts only, and the expense of other methods of separation would undoubtedly be prohibitive. It is possible that a segregation of the potassium might be accomplished with a partial elimination of other salts. A large expenditure, reported to be upwards of a million and a quarter dollars, has not yet resulted in a commercial production from this source. One crystallisation procedure has been tried out on a large scale and abandoned. It is reported that the present occupants of the site, the Trona Company of California, are trying out another process, the essential features of which are a saturation of the brine with carbon dioxide and the freezing out of carbonates and boricates by reducing the temperature of the mother-liquor with an ordinary ice-making outfit. The scheme is an ingenious one, but its practicability in the middle of a large desert seems questionable in the absence of fuller details of this company's plans.

Another difficulty menacing the production of potash salts at Searle's is the validity of the titles of the present

possessors. The Trona Company is controlled by a British corporation, the Consolidated Gold Fields of South Africa, and its holding is the largest ever taken over in the United States by any one individual or company; consequently protestants have arisen, and it is claimed that the original patents on which the title rests were obtained fraudulently. Interested parties claim the possibility that the title of the Trona Company will be rejected and the site withdrawn from entry pending the passage by Congress of a leasing law. Be this as it may, the uncertainty has hampered and is hampering the development of the property. It seems to be the best opinion of disinterested investigators that ultimately Searle's Lake may be worked as a source of trona (sodium bicarbonate), with borates and potassium salts as by-products. The production of potassium will be relatively small as compared with the country's needs. Opinions differ as to the probable grade of the potassium salt. The present writer thinks it must be a low-grade one.

Alunite.

Near Marysville, Piute County, Utah, there is a large deposit of massive alunite, an insoluble mineral, with the composition of a basic potassium aluminosulphate. It is quite similar in composition to alum; hence its name. Other occurrences of alunite in the United States are known, but this is the only one where the mineral occurs in such form and such quantities as to make it a commercially workable proposition. When roasted, sulphur dioxide and sulphur trioxide are volatilised, and if the residue be leached either alum or potassium sulphate is extracted, depending primarily upon the temperature of the roasting. The Roman alum, long a commercial product, is thus obtained from Italian alunite, and it has been reported that deposits in Spain, Italy, Australia, and Japan have at times been small producers.

The technical difficulties in producing potassiums from alunite are not serious, but the deposit is located in a forest reserve. The oxides of sulphur if allowed to escape into the air may damage vegetation and bring objection from Federal authorities; if condensed and discharged into the streams they will be a menace to fish life, and thus bring objection from State authorities. Sulphuric acid produced in Southern Utah has no obvious market in normal times; hence, what might be an asset in some localities, bids fair to be a serious charge on the working of the Utah alunites. The residue after leaching is a very fair grade of alumina, and possession of a large source of alumina has long been a fairer vision to the lay chemist than ownership of a gold mine. However, there is but one large purchaser of alumina in the United States, and this purchaser has spent great energy, time, and money in securing to itself the more important deposits of bauxite; hence it cannot be expected to look with enthusiasm upon the development of another considerable source of alumina. For the Utah operators themselves to undertake to produce aluminium appears to be impracticable, for reasons which need not be discussed here. Other possible uses of the alumina are receiving serious attention, but are as yet of doubtful importance, as a sufficient outlet for the quantity of material for which disposition is desired.

The most serious difficulty affecting the production of potassium sulphate from alunite is the transportation problem, incident to the geographical location of the alunite deposit. The sulphate of potassium is the form most favoured by agricultural authorities, it is true, and in normal times this is the form of "potash" which should command the readiest and largest market. West of the Mississippi River the citrus region of Southern California is the only important market in the United States, and of especial interest because it will not use chlorides but readily takes a fair amount of the sulphate. Hawaii and Japan are certainly possible markets to be considered. The mountains of Southern Utah are about as unfortunate a location as could well be imagined, since the potassium salt must expect a long rail haul to any important market.

In spite of these difficulties the exploitation of the alunite has been progressing. By far the major part of the material is in the control of two holders. The Mineral Products Company, having close affiliations with one of the largest fertiliser manufacturers in the country, has established a small plant near Marysville, and has recently produced potassium sulphate on a commercial scale. It is too soon perhaps to form any definite opinion on the probable success of this venture. The European war has introduced factors which are difficult to evaluate, and, moreover, the entire output of the venture is in the hands of one purchaser, so that the crucial test of the open market is not available.

The Utah Potash Company, a recently organised corporation for the working of the alunite deposits on the holdings of the Florence Mining and Milling Company, is maturing plans for a large installation near Marysville, proposing to work under the Morgan patents, roasting the alunite with lime, whereby a lower temperature can be employed profitably and the escape of the objectionable oxides of sulphur is prevented. The plans of this company are predicated on the experience of copper gold, and other mining ventures where a low-grade ore worked on a large scale is often very profitable when it is a commercial impossibility on a small operation. In fine, potassium salts have been produced from alunite in the United States, and there is a very good promise that they will continue to be produced from this source, even when they come into competition with the German salts following the close of the war.

Among the considerable number of sea algæ on the Pacific Coast of North and South America occur four species which are peculiar to that coast, and which have the power of absorbing from the sea-water exceptionally large quantities of potassium. Of these four algæ, or Giant Kelps, as they are known locally, *Macrocystis pyrifera* is undoubtedly the most important. It reaches its best development south of Point Sur, on the California coast, and north of the Cedros Islands, off the coast of Mexico, where it occurs in large beds or groves, from a few acres in extent to fifteen square miles or more. The entire kelp beds along the coast of the United States and Alaska aggregate 400 square miles or more, and could be made to yield annually under careful harvesting some six or seven times the normal demands of the United States. The California beds alone could easily produce more than our present normal requirements.

The *Macrocystis* plant when freshly harvested contains from 3 to 5 per cent potassium chloride. The oven-dried plant will average probably 16 per cent potash (K_2O) in the form of chloride. The dried plant also contains something less than 2 per cent nitrogen, and being fibreless it goes to pieces in the soil quickly and readily. Pot and garden experiments with dried kelp have shown it to be an excellent fertiliser as compared with equivalent amounts of the ordinary soluble potassium salt.

Harvesting of kelp on a scale comparable with commercial conditions has now been done by a sufficient number of different investigators to have definitely demonstrated the practicability and low cost of the operation. The cost of drying artificially the harvested product has not been worked out so satisfactorily, but enough has been done to show that it is very probably feasible as a commercial operation when the technology of the operation has been adapted to the peculiar characteristics of the material adaptations, which will speedily come with more practice and actual contact with the material. Apparently a modern rotary drier is the type most promising, since the wet kelp, when heated in a furnace where a stirring is not provided, quickly mats down to a sticky mass, from the surface of which potassium chloride may be volatilising, while at the same time the wet interior is at a temperature quite durable to the hand.

While dried kelp is itself a good fertiliser and seems admirably adapted to use in mixed fertilisers, and can probably be produced at a cost which would ensure a good

profit on the basis of before-the-war prices, it is possible that kelp ash may be more worthy of consideration for the Eastern market. In this material naturally there is no nitrogen, but there is about 60 per cent potassium chloride, the remainder being mainly sodium chloride; but it is as a source of pure potassium chloride that kelp has the most promising future. The kelp ash contains, when not too severely burnt, very little soluble material other than potassium and sodium chlorides. Theoretical deductions backed by laboratory experiments have shown the feasibility of a separation of true salts by treating a fixed mass of water with easily calculated amounts of the particular ash, at alternate temperatures, whereby there is a practically complete recovery of the potassium chloride in a nearly pure condition. The writer's own observation and studies have convinced him that these giant kelps offer by far the cheapest and most feasible source known for the production of a practically pure potassium chloride in very large quantities.

But while the future of the potassium sulphate from alunite appears with almost a certainty to lie in fertilisers, and in a minor degree as a raw material for the production of potassium carbonate, a pure potassium chloride from kelp would probably find quite different openings. Undoubtedly some of it would be utilised in fertilisers, but mainly it would be used in the production of potassium chlorate. Potassium chlorate is the basis for a type of "permissive" explosive much favoured by construction engineers in the West, and growing in favour everywhere. It is probable that a big impetus will be given to its use by the favour which it has found in the present war, but it is particularly as a necessary raw material in the production of safety matches that it is desired. This country could and probably would soon become the largest producer of safety matches with a satisfactory development of the kelp industry.

It seems desirable here to point out that while there may be useful by-products from kelp developed some time in the future, there is no great promise of such in sight at the present time. The oft heralded promise of cheap iodine is purely illusory. The main, practically the only, commercial source of iodine in the world to-day is the mother liquor from the crystallisation of Chili saltpetre; but only about one-twelfth of the possible yield of iodine from this source is recovered in peace times simply because the world's demands are thus fully satisfied, and the cost at which iodine can be produced in Chili would make it impracticable to recover it from the kelp, though there are no serious technical difficulties in so doing.

The *Macrocystis* has a life-history longer than one calendar year. It is probably a perennial. Moreover, harvesting it to a moderate depth appears to produce a stooling effect, causing it to grow more thickly and heavily. As the average length of a full-grown plant is about 100 feet, from 30 to 70 feet of the plant's length is streaming along near the surface with the tide or wind, and a cutting of four to six feet leaves no noticeable effect upon the harvested area; consequently it seems probable that several cuttings a year can be made without damage to the bed. Indeed, observations on harvested areas indicate a decided improvement in growth is likely to ensue.

The beds all lie within the one marine league limit; hence control of them is vested in the State and not in the Federal Government. There appear to be no State laws applicable. Capital is notoriously timid of competition, and competition, even to the harvesting of the same bed by rival interests, is quite possible now, legally as well as physically. Moreover, however unfounded the fear may be, there has been a very real fear on the part of capital, in the absence of any pertinent laws, that it might become the victim of unfriendly legislation, and there has been a very real fear of the possibility of trouble from unscrupulous individual legislators. It has been the lack of adequate State legislation that has been and is yet the principal bar to the development of a potash-from-kelp industry.

Small amounts of dried kelp, kelp ash, and high-grade potassium chloride have been produced. One operator produced in all something over twenty tons of potassium chloride, but the company was improperly financed, was the victim of improper promoting and wild-cat stock jobbing, and was forced because of its financial difficulties to come to a stop just when it had demonstrated its ability to produce a high-grade product at a cost ensuring a profit.

Summary.

From the foregoing it appears that there are within the United States large stores of raw materials from which it is possible to obtain ample supplies of potash salts; that the technology of the subject is sufficiently developed to demonstrate the entire practicability of a supply from native sources, so far as physical factors are concerned. We can have "potash" if we really want it and are willing to pay for it. There are, however, serious commercial doubts affecting each of the four possible sources, and concerning the validity of these doubts opinions may well differ. Those most familiar with the problem are the most sanguine of the probability of commercial success.

While it is undoubtedly true that governmental efforts can yet furnish assistance, there is a very serious doubt as to how far these efforts should be continued. The time seems to have arrived when the commercial interests should themselves squarely assume the tasks confronting them and the costs of what further experimenting is necessary. This they have been slow to do, but there is rapidly accumulating evidence that these interests are responding to the spur of necessity, and that sooner or later potash salts from American sources are to be upon the market. An early cessation of the European war might delay but can no longer stop the development of our potash resources.—From the *Journal of the Franklin Institute*.

SIMPLE FOOD TESTS.

EXPERIMENTS BY WHICH ADULTERANTS MAY BE DETECTED.

By S. LEONARD BASTIN.

A VERY good test by means of which the best fresh butter may be distinguished from the made-up article or margarine is that in which a small quantity of the sample is placed in a tiny tube. This is set in water sufficiently warm to melt the contents; the sample is kept in a melted state for half-an-hour, and it is then examined. If the butter is pure and of the highest quality, it will almost certainly be clear. On the other hand, with margarine or a worked-up butter a certain cloudiness will be apparent. A more simple, but equally reliable test, is that in which a piece of the suspected article about the size of the tip of the little finger is placed in a spoon. This is held over a gas-burner, and the behaviour of the sample is watched. Real butter boils quietly, producing a quantity of small bubbles; on the other hand, margarine, or a process butter, will crackle and sputter much in the way that green leaves do when they are placed on a fire.

Two simple tests for tea and sugar are indicated. One of the commonest adulterations of tea is the dyeing of the leaves to make them look a good colour. The fraud is very easy to detect. Get a clean white cloth and rub some of the dry leaves between the material. Pure tea which has not been treated should leave no mark on the cloth; dyed tea will make a very definite stain that will not easily be rubbed away.

Several additions are now and again made to sugar, and, without an elaborate analysis, it is not easy to determine the exact nature of these. As a rule, pure sugar should answer the following test satisfactorily. Make an almost saturated solution of sugar and water; place this in a glass-tube; then stand in front of some print. It should be possible to read the type quite clearly through the sugar solution. In the case of brown or raw

sugars there might be a certain amount of discoloration of the water, though any turbidness is almost certainly an indication of adulteration.

An unscrupulous baker will work into his bread as much salt as possible. Experts say that an increasingly large amount of salt may be put into bread without the consumers being aware of it. The idea is that bread loaded with salt weighs more heavily on account of the moisture which it will retain. To find out the real value of bread from the standpoint of weight a little experiment may be followed. Take two samples of equal weight, and bake these in an oven for an hour. At the end of this time weigh again. That which is the heavier is the better value. The addition of alum to bread to make it white (often used to mask an inferior flour) is much to be condemned. Small quantities of alum taken regularly in this way are very harmful. Happily a simple test for the discovery of alum in bread is available. Take a sample of the suspected article and place it in a saucer. Then pour over it a solution of carbonate of ammonia. If alum is present in the bread it will turn black, but if the bread is pure no change will take place.

A large amount of jam is dyed; brightly coloured articles should always be suspected. The point may be definitely established in this way. Mix a sample of the jam or jelly with an equal quantity of water. Throw into the mixture a piece of cotton-wool, and boil for half-an-hour. Now try to wash out the stain. If the jam is pure the stain can be easily removed; where dye has been used no amount of washing will get rid of the stain.

Finally, a good test for vinegar may be described. In this case a common adulteration is the addition of some mineral acid. The presence of the harmful article is readily disclosed. Take a sample of the vinegar and add a few drops of methyl aniline violet. Pure vinegar shows no alteration, but the adulterated sample turns a blue or a green colour.—*Scientific American*, cxiv., No. 4.

ON THE PREPARATION OF GLYCOLL AND DIETHYL CARBONATE.

By W. A. DRUSHEL and D. R. KNAPP.

THE preparation of glycoll by the interaction of ammonia and chloracetic acid is attended by by-reactions which make it impossible to obtain a quantitative yield of the amino acid. In 1858 Perkin and Duppa (*Quart. Journ. Chem. Soc.*, xi., 22) obtained a small yield of glycoll by the action of ammonia upon bromacetic acid at the boiling temperature; later Cahours (*Comptes Rendus*, xvi., 1044; cvii., 147), repeating the experiment with chloracetic acid, got a yield of 10 per cent to 15 per cent. Mauthner and Suida (*Monatsh.*, xi., 374) improved the yield by working with ammonia and chloracetic acid in the cold, and more recently Kraut (*Ann. Chem. Pharm.*, cclxvi., 299) was able to get a yield of 50 per cent to 55 per cent by cooling the reaction mixture to 10°. The very marked improvement in yield obtained by Kraut suggested the possibility of even a better yield by working at 0° and keeping the reaction mixture saturated with ammonia until all of the chlorine was fixed as ammonium chloride.

In this investigation 700 cc. to 800 cc. of ammonia water were cooled to 0° in an ice bath, and saturated at this temperature with gaseous ammonia. One hundred grms. of chloracetic acid were dissolved in the least possible amount of water and slowly run into the ice cold saturated solution of ammonium hydroxide, keeping the reaction mixture at 0°, and saturated by passing gaseous ammonia. In our earlier experiments the mixture was kept at 0° for about fifteen hours and was then allowed to stand at room temperature for several days. In the later experiments the temperature was kept at 0° for more than four days; the reaction was found to go to completion at this temperature in about five days. The velocity of the

transformation of the chloracetic acid was determined by pipetting off 5 cc. portions of the reaction mixture from time to time, neutralising the excess of ammonia with ice cold nitric acid, and titrating the ammonium chloride present with standard silver nitrate, using potassium chromate as an indicator. A good concordance in velocity constants was obtained by making the calculation from the usual formula for second order reactions. The mean of a series of five velocity constants is 0.000223. The glycol was recovered from the reaction mixture and purified by the copper hydroxide method; the use of copper carbonate instead of copper hydroxide suggested by H. T. Clarke, ("Organic Chemistry," 290) was also tried, but was found to be much less satisfactory than copper hydroxide. In no case did the yield of pure glycol exceed 55 per cent of the chloracetic acid used. It does not seem possible to increase the yield of glycol by changing the conditions of Kraut's method in the direction of lowering the temperature or increasing the concentration of ammonia during the reaction.

Diethyl Carbonate.—Since cyanformic ester is readily converted into aminoacetic ester by reduction, it seemed desirable to examine the methods of preparing cyanformic ester. In 1895 Neff (*Ann. Chem. Pharm.*, cclxxxvii., 308) obtained this ester mixed with some diethyl carbonate by the action of potassium cyanide upon chlorformic ester in 25 per cent aqueous alcohol at -13° , allowing the temperature to rise slowly during the course of the reaction to -2° . Under these conditions only about 50 per cent of the chlorformic ester was converted into cyanformic ester. In our experiments absolute alcohol was used, resulting in the abundant formation of diethyl carbonate without any cyanformic ester. Powdered potassium cyanide was covered in a flask with absolute alcohol, and then one equivalent of chlorformic ester mixed with an equal volume of absolute alcohol was slowly added in small portions through a reflux condenser under a good draught hood. Heat was evolved, hydrocyanic acid was given off, and the reaction mixture became red in colour. The mixture was finally boiled for an hour on the water bath to bring the reaction to completion. The residue was then filtered off and the filtrate was fractionally distilled. The first fractionation gave almost pure diethyl carbonate, probably according to the equation $C_2H_5CO_2Cl + KCN + C_2H_5OH = (C_2H_5)_2CO_2 + HCN + KCl$. After redistillation the product boiled at 127° , and its identity as diethyl carbonate was further established by determining its molecular weight; by determining its saponification equivalent as 59, its specific gravity as 0.968 at 25° ; and finally by preparing urethane from the product by the action of ammonia.

No cyanformic ester could be isolated from the reaction mixture and the yield of diethyl carbonate after purification was 50 per cent of the chlorformic ester used.—*American Journal of Science*, 1915, xl., 509.

THE EXEMPTION FROM ENLISTMENT OF ANALYTICAL, CONSULTING, OR RESEARCH CHEMISTS.

IN order to clear up any misunderstanding that may arise in consequence of recent legislation concerning Reserved occupations, the Royal Society desire to point out that an unmarried chemist of military age entitled to exemption as an "analytical, consulting, or research chemist" should, unless he has been attested before March 2, lodge a claim for exemption with the Local Tribunal before that date.

Men who have been attested should lodge their claims for exemption with the Recruiting Officer or Local Tribunal when called up for enlistment, and if such claims be not admitted, a communication, stating all material facts in favour of the disputed claim, should be addressed at once to the SECRETARIES of the Royal Society, Burlington House, London.

THE SEPARATION AND ESTIMATION OF ALUMINIUM AND BERYLLIUM BY THE USE OF ACETYL CHLORIDE IN ACETONE.

By H. D. MINNIG.

IN a former paper from this laboratory (*American Journal of Science*, 1915, xxxix., 197), a method was described for the quantitative separation of aluminium from iron by the use of acetyl chloride in acetone. The application of this method depends on the fact that from concentrated aqueous solution of the two chlorides aluminium is precipitated completely as the hydrous chloride, while the iron remains in solution. This precipitation is brought about, doubtless, by the decomposition of the acetyl chloride and simultaneous formation of hydrochloric acid, which, as is well known, is a precipitant for aluminium. At the same time the precipitating mixture furnishes organic liquids in which the precipitated hydrous chloride of aluminium remains insoluble and the chloride of iron soluble. The main function of the acetone is simply to abate the violence of the reaction which ensues when acetyl chloride reacts with water.

Commercial acetyl chloride cannot be used in this work because of phosphorus compounds used in its manufacture, the last of which cannot be removed. This phosphorus contamination shows itself not only in the filtrate from the aluminium precipitate, but also in the aluminium precipitate itself, giving high results. The acetyl chloride was therefore prepared as described in the former article (*loc cit.*). Acetic anhydride was distilled from a little anhydrous sodium acetate to remove contaminating phosphorus compounds. Tests for included phosphorus compounds were made by hydrolysing the acetic anhydride with water, evaporating down with nitric acid to oxidise any trivalent phosphorus which might be present from the manufacture of the commercial product, and treating the solution with ammonium molybdate in nitric acid solution. The purified acetic anhydride was then saturated with hydrogen chloride and the product distilled at $100^{\circ}C$. in a rapid current of the same gas. Re-distillation gives pure acetyl chloride.

The method of procedure was the same as in the separation of iron from aluminium. Measured portions of solutions of the two chlorides in small beakers were evaporated to the smallest possible volume on the steam bath. In case the evaporation proceeds to dryness it is well in dissolving the salts to add a drop of hydrochloric acid to prevent the formation of basic salts, particularly of basic beryllium chloride. The beaker containing the concentrated solution was then placed in a dish of cold water and the acetone-acetyl chloride mixture (4:1) was added drop by drop from a dropping funnel to the complete precipitation of the hydrous chloride of aluminium. Fifteen to twenty cubic centimetres of the mixture usually sufficed. The settling of the crystalline precipitate is a good indication, though not an infallible one, of the complete precipitation of the aluminium chloride. When the precipitation was judged to be complete, the precipitate was transferred to a weighed perforated platinum crucible and carefully washed with the precipitating mixture. The filtrate and washings were caught in a beaker under a bell-jar. The precipitate was dried slowly, at first high above a low Bunsen flame and then gradually lowered until the full heat of the burner was obtained. The hydrous chloride on ignition leaves the oxide. The acetone-acetyl chloride solution of beryllium was copiously but cautiously diluted with water to avoid spattering, and the resulting solution in a beaker covered by a watch-glass, was warmed gently on the steam bath until the volume seemed to remain constant, indicating that the easily volatile acetone had been removed. The solution was then boiled and ammonium hydroxide added to alkaline reaction. The precipitate was allowed to settle, filtered, and treated as usual in determinations where beryllium is weighed as the oxide. Results of the experiments are given in Table I.

TABLE I.—Separation by One Precipitation.

Al ₂ O ₃ taken as AlCl ₃ . Grm.	Al ₂ O ₃ found. Grm.	Al ₂ O ₃ error. Grm.	BeO taken as BeCl ₂ . Grm.	BeO found. Grm.	BeO error. Grm.
0.0927	0.0933	+0.0006	0.0638	—	—
0.0927	0.0934	+0.0007	0.0638	—	—
0.0927	0.0943	+0.0016	0.0638	—	—
0.0927	0.0934	+0.0007	0.0638	—	—
0.0927	0.0937	+0.0010	0.0638	—	—
0.0865	0.0878	+0.0013	0.0561	0.0549	-0.0012

High results in Table I. seemed to indicate that beryllium chloride was being included in the aluminium precipitate, a circumstance which does not seem surprising in view of the marked similarity between the reactions of the two elements. A double precipitation of the aluminium was therefore tried. After the first precipitation the liquid was decanted through the filter, retaining as much as possible of the precipitate in the beaker. This precipitate in the beaker was washed four or five times with the precipitating mixture and finally dissolved in a small quantity of water. The excess of water was evaporated off and the process of precipitation repeated. The two filtrates were united and the beryllium determined as before (Table II.).

TABLE II.—Separation by Two Precipitations.

Al ₂ O ₃ taken as AlCl ₃ . Grm.	Al ₂ O ₃ found. Grm.	Al ₂ O ₃ error. Grm.	BeO taken as BeCl ₂ . Grm.	BeO found. Grm.	BeO error. Grm.
0.0865	0.0869	+0.0004	0.0561	—	—
0.0865	0.0868	+0.0003	0.0561	—	—
0.0865	—	—	0.0561	0.0564	+0.0003
0.0865	0.0867	+0.0002	0.0561	0.0575	+0.0014
0.0865	0.0867	+0.0002	0.0561	0.0561	—
0.0865	0.0865	—	0.0561	0.0560	-0.0001
0.0865	0.0870	+0.0005	0.0561	0.0554	-0.0007
0.0865	0.0866	+0.0001	0.0561	0.0557	-0.0004
0.0865	0.0881	+0.0016	0.1122	0.1111	-0.0011
0.0865	0.0884	+0.0019	0.1122	0.1093	-0.0029
0.0865	0.0869	+0.0004	0.1122	0.1118	-0.0004
0.0865	0.0873	+0.0008	0.1122	0.1108	-0.0014
0.1730	0.1739	+0.0009	0.0561	0.0548	-0.0013
0.1730	0.1741	+0.0011	0.0561	0.0554	-0.0007

That there is danger of inclusion of beryllium chloride could readily be seen when the quantity of that substance was increased. Unless the progress of the precipitation was watched and the addition of the precipitating mixture stopped as soon as the separation of the crystalline aluminium chloride seemed to be complete, beryllium chloride could also be seen to separate out (probably the same compound mentioned on page 24 of Parson's book, "The Chemistry and Literature of Beryllium"; that precipitate was obtained by the use of ether saturated with hydrogen chloride). Its appearance is very unlike that of the aluminium chloride and can easily be distinguished. Even when the addition of the precipitating mixture was stopped before the formation of this salt became noticeable in the beaker, it appeared as soon as the supernatant liquid had been poured through the filter and an attempt was made to wash the precipitate. Increase in the quantity of aluminium chloride seems also to have a like effect because of the necessity for an increased volume of the precipitating mixture.

The comparative insolubility of beryllium chloride in acetone acetyl chloride (4 : 1) limits this process therefore to separation of quantities of the two elements present as the chlorides which do not exceed the equivalent of 0.15 gm. of the oxides. Of this amount beryllium oxide should not greatly exceed one-third.

The use of acetyl chloride as a substitute for hydrogen chloride simplifies very much the method of Havens (*Am. Journ. Sci.*, [4], iv., 111), and therefore the

favourable criticism of Noyes, Bray, and Spear ("A System of Qualitative Analysis for the Common Elements," III., 19) ought to apply to this method as well as to that of Havens. These investigators found the method of Havens to be very reliable even when the amount of aluminium present was exceedingly small.—*American Journal of Science*, xl., 482.

INSTITUTE OF INDUSTRY (OF GREAT BRITAIN AND IRELAND) LIMITED.

THE Institute of Industry has appointed a Special Committee of its Court of Directors to meet representatives of important trade interests with a view to considering suggestions having for their purpose the strengthening of the Court of Directors, and the co-operation or amalgamation of other similar movements. The Committee appointed is as follows:—

F. J. Nettlefold, Esq. (Chairman).

Sir Clifford J. Cory, Bart., M.P. (Messrs. Cory Bros. and Co., Ltd.).

Sir James Heath, Bart. (Messrs. R. Heath and Sons, Ltd.).

Godfrey C. Isaacs, Esq. (Managing Director, Marconi Wireless Telegraph Co., Ltd.).

Frank Warner, Esq. (President, the Silk Association of Great Britain and Ireland).

The Directors propose to take advantage of the suggestion put forward in this direction by Sir Edward Carson at their recent luncheon at which he was the principal speaker, and a number of business men have promised to subscribe the requisite funds to ensure success.

It is gratifying to learn that developments of a far-reaching nature are now pending, and that it will not rest solely with the House of Commons, as it has in the past, to determine the economic future of the country.

There has been a considerable increase in the membership of the Institute since the beginning of the year, and in order that the position may be still more strengthened the Directors would be glad if British manufacturers and other gentlemen interested in the industrial welfare of the United Kingdom and the Empire would send in their applications for membership to THE SECRETARY, Institute of Industry, Aldwych Site, Strand.

The Queensland Agricultural Chemist.—The varied duties of the agricultural chemist have been enlarged by the operations of the Pure Seeds Act, which have been placed under his charge, and his difficulties have been added to by the scarcity, owing to the war, of glassware. This scarcity is also a great inconvenience to the butter factories, which use a considerable quantity each year, and evidence is given by the reduction by 432 in the number of glassware tested under the Dairy Produce Acts as against 1913-1914. The range of analyses is wide, and reference to the report will show 25 different items scheduled in addition to the seed-testing; in all 1564 analyses were made, 3721 articles of glassware, and 467 different lots of seed were tested. An interesting investigation has been made by Mr. Brunnich into the fertility of soils, some of which, after having been cropped for many years, show good fertility. A collection of samples of limestones from various parts of the State have provided valuable information that will be of great use when farmers decide, as they should do, to use, to a much greater extent than they now do, lime. Among the waters tested an interesting discovery was made that a water that caused mortality among pigs contained a high nitrate content, amounting to about 170 grains of saltpetre to the gallon.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 10, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Theory of the Helmholtz Resonator." By Lord RAYLEIGH, O.M., F.R.S.

The ideal form of a Helmholtz resonator is a cavernous space enclosed in a thin immovable wall, but communicating with the external atmosphere by means of a small perforation. An approximate theory is due to Helmholtz, who arrived at definite results for apertures whose outline is circular or elliptic.

In the present paper the approximation is carried further for the special case where the wall is spherical, with the aid of the appropriate Legendre's functions. When the escape of energy to a distance is neglected, the wave-length (λ) of plane waves having the period of the resonator is given by—

$$\lambda = \pi v(2S/R) \cdot \left\{ 1 - \frac{9}{1} \frac{R}{2\pi C} \right\},$$

where C is the radius and S the volume of the sphere, R the radius of the circular aperture. It is shown that the result may be extended to elliptic apertures, however great the ellipticity.

An imaginary term in λ provides the means of estimating the rate at which the vibrations decay. The result differs somewhat from that arrived at in "Theory of Sound," § 311, where the aperture is supposed to be surrounded by an infinite flange, the effect of which is to favour the propagation of energy away from the resonator.

"Oxyhydrogen Flame Spectrum of Iron." By Sir NORMAN LOCKYER, F.R.S., and H. E. GOODSON.

A spectrogram of the light emitted when metallic iron burns in the oxyhydrogen flame, notably rich in lines due to the metal, has been studied. Sixty-four lines of iron have been identified in the region $\lambda\lambda$ 3856.52—5615.88. Fifteen of these lines do not appear to have been hitherto recorded in the iron-flame spectrum, and a number of these latter possess special interest.

On the basis of a comparison of the flame spectrogram with a spectrum of the iron arc of approximately similar exposure, it has been possible to separate the flame lines according to the observed variations of intensity into two well-marked groups, whilst a residuum forms an intermediate group. All the flame lines have accordingly been placed in one or other of the following three groups:—

- Group A containing lines stronger in flame than arc.
- " B " " weaker " "
- " C " " nearly equal in both sources.

This division bears close relation to the more minute classification employed by King in the case of spectra obtained at varied temperature levels in the electric furnace. A point of special importance is the number of lines of King's Class IA now recorded present in the flame spectrum.

Data published by Adams show the lines in Group A are very much stronger in the flame of the arc than in the core, and all these lines are strengthened in some spot spectra.

In stellar spectra the initial appearance and maximum development of the lines of Group A occur at later stages than for the lines of the other groups.

"Consumption of Carbon in the Electric Arc. III. The Anode Loss." By W. G. DUFFIELD and M. D. WALLER.

It has already been shown that the rate of consumption of carbon from the cathode of a very short arc is such that the departure of one atom is accompanied by the transfer between the poles of four electronic charges.

The above experiment gave a clue to the rôle played by the cathode. The following experiments were undertaken to determine the part played by the anode.

An experiment described in the earlier paper was repeated in the following manner:—

A carbon rod 18 mm. diameter was rotated in a lathe and an arc started between its curved surface, and a pointed carbon rod which formed the cathode, and which could be moved rapidly to and fro along the anode. In this way the anode remained fairly cool, and the crater did not have time to develop. Anode and cathode were weighed before and after each experiment. Whereas in the stationary form anode loss was invariably greater than cathode loss, with rotating anodes the total losses from the anode for currents of 4, 6, 8, and 10 amperes after running the arc for five minutes were only 3, 2, 8, and 13 mgrms. respectively. The ratios of the consumption of carbon per coulomb for fixed and rotating anodes for these current densities being 17.6 to 0.25, 13.5 to 0.13, 12.8 to 0.33, and 10.8 to 0.36 respectively.

It appears that the anode loss of carbon is unimportant in the mechanism of the arc, and that the function of the anode is to receive the carriers of the current produced by the essential process occurring at the surface of the cathode. The formation of a crater in the normal type is not vital to the arc, though it is its most prominent feature.

The reduction in potential difference in the arc with rotating anode is probably due to absence of electronic emission on a large scale from its cooler anodes.

"Surface Friction. Experiments with Steam and Water in Pipes." By C. H. LANDER.

The work comprises a verification of Rayleigh's formula connecting resistance with velocity, density, diameter of pipe, and kinematical viscosity of fluid.

Experiments were carried out on three wrought-iron pipes of diameter 3.30, 1.905, and 1.07 cm. respectively, water and steam being used as moving fluids.

The range extended from water velocities of 50 cm. per sec. to steam velocities of 6400 cm. per sec., and steam pressures from 0.8 kg. per sq. cm. to 15 kg. per sq. cm.

All resistances measured have been corrected to that obtaining in the initial unit-length of pipe, and, where necessary, corrections have been applied to allow for increments of pressure necessary to accelerate the steam from initial velocity to final velocity.

A curve has been plotted with values of $R/\rho v^2$ as ordinates and of $\log vd/v$ as abscissæ. The results are slightly above those obtained by Stanton and Pannell for water and air in brass pipes, and show similar characteristics. For high values of vd/v a limit has apparently been reached where resistance varies as square of velocity for the particular roughness of surface in the experimental tubes.

The general results of the work confirm the accuracy of the assumptions made in the derivation of the equation—

$$R = \rho v^2 F\left(\frac{vd}{v}\right)$$

for fluids differing as widely in their properties of viscosity, density, &c., as steam and water.

"Structure of Broadened Spectrum Lines." By T. R. MERTON.

It is considered improbable that the broadening of spectrum lines which occurs at high pressures and under conditions of powerful electric discharge can be referred to the movement of the atom as a whole, but rather to processes more intimately connected with the problem of radiation. Stark has suggested that the broadening is closely related to the electric resolution of the lines. On this assumption the distribution of intensity to be expected in the lines $H\alpha$, $H\beta$, and $H\gamma$ of hydrogen, broadened by powerful discharges, is discussed. A method of investigating the distribution of intensity in these broadened lines has been found. This method is not affected by the eccentricities of the photographic plate, and is adapted to

quantitative measurements. The results for the hydrogen lines shows that $H\alpha$ consists of a strong maximum falling off rapidly and regularly on either side. $H\beta$ falls off much less rapidly, and shows a minimum at the centre of the line, and $H\gamma$ shows a strong central maximum with very diffuse "wings" on either side. These results are in agreement with the distribution of intensity deduced from the electrical separation of the lines.

NOTICES OF BOOKS.

Water Purification Plants and their Operation. By MILTON F. STEIN, Assoc. Mem. Am. Soc. C. E. Pp. 258. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1915.

THIS book will be a valuable aid for chemists who are employed at water purification plants, especially those who have charge of small plants and who have not had the advantage of advanced technical training. The special difficulties which the young chemist meets with in adapting his knowledge acquired in laboratory work to the somewhat different conditions of actual practice have been well kept in mind. The first chapter contains some account of the composition of natural waters and discusses the origin of the various substances to be found in them; a geological map of the United States is provided, and a brief general account is given of the pollution of streams by sewage and mine drainage. Various types of purification plants used in America are then described in detail. In a chapter on physical and chemical tests the usual daily examination of the raw and purified water is described, full directions being given for carrying it out so as to ensure accuracy. Practically no previous knowledge of chemistry is assumed; details for making up standard solutions are given in an appendix, but the inexperienced are recommended to get them ready prepared. The chapter on bacterial tests will be found a useful guide, although the chemist who had had no training whatever in bacteriology would possibly find himself rather at a loss if he had to rely upon the information in it alone. Processes employed for coagulation, sterilisation, and softening are fully treated, and a very useful portion of the book is devoted to the discussion of details of organisation in water purification plants, the routine work of the chemists employed, and the keeping of records and collection of statistics.

The Urgency of a Definite Forward Movement in the Study of the Active Principles of South African Plants. By F. F. JURITZ, M.A., D.Sc., F.I.C. Cape Town: Townshend, Taylor, and Snashall. 1915.

THIS paper was read before the British Medical Association at a meeting of the Cape Town (Western) Branch in August, 1915, and has been reprinted from the *South African Medical Record*. The author, after pointing out the great need for research on the subject, for which South Africa is an ideal place, traced the manner in which our present knowledge has developed. A list is added giving the active principles, classified according to chemical composition, which are known to exist in various plants.

The British Journal Photographic Almanac, 1916. London: Henry Greenwood and Co., Ltd., Wellington Street, Strand.

THE *Photographic Almanac* is so well known that an introduction is unnecessary. The editor, George E. Brown, F.I.C., is to be congratulated upon having kept the Annual quite up to its usual value in spite of the present unsettled state of things. The interest is even greater than usual, for the occasion has been used to give a

survey of the resources of Great Britain in the production of the requisites for photography: the fifty pages occupied upon this subject show clearly that we are quite capable of producing all that is necessary in chemicals, lenses, or apparatus, and that manufacturers are ready to take the opportunity that the war is affording for home production.

A lengthy article by the editor upon Printing Processes is interesting reading and deals with the subject very completely, and there is the usual budget of hints and dodges for photographic manipulation. The book runs to nearly 1000 pages, and will be welcomed by all who practise the art of photography.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 25, December 20, 1915.

Series of Triamino-aquo Salts of Divalent Platinum, $(Pt_3NH_3 \cdot H_2O)X_3$.—L. Tschugaeff and I. Tschernjaeff. —When a current of air is passed through a solution of the chloride, $[NH_3 \cdot OHNH_2PtNH_3 \cdot OHNH_2]Cl_2$, containing ammonia, ammonium sulphate, and a small quantity of some copper salt it undergoes oxidation, and a colourless crystalline precipitate is obtained. This precipitate is soluble in dilute sulphuric acid, and a solution gives with a soluble chloroplatinite a green crystalline precipitate of $[Pt_3NH_3 \cdot H_2O]PtCl_4$. A perfectly analogous bromoplatinite can be obtained similarly.

No. 26, December 27, 1915.

This number contains no chemical matter.

Vol. clxii. No. 1, January 3, 1916.

New Series of Platinum Compounds Analogous with Cossa's Salts.—L. Tschugaeff and W. Lebedinski.

—When acetonitrile acts on potassium chloroplatinite a salt analogous with Cossa's double salt, $Pt_4NH_3[PtCl_3]_2$ is obtained. The authors have shown that acetonitrile has the same action on soluble chloroplatinites as ammonia and the organic amines.

MEETINGS FOR THE WEEK.

TUESDAY, 29th.—Royal Institution, 3. "The Plant and the Soil—Nature's Cycle," by Dr. E. J. Russell.

WEDNESDAY, March 1st.—Society of Public Analysts, 8. "Manufacture of English Chemical Filter-paper," by E. J. Bevan and W. Bacon. "Pink Colour on the Surface of Margarine," by A. W. Knapp. "Rapid Method for the Estimation of Fat in Powders," by S. B. Phillips. "New Colour Reaction for Ales," by C. E. Stacy.

THURSDAY, 2nd.—Royal Institution, 3. "Recent Excavations in Mesopotamia—The Northern Capitals, Nineveh and Ashur," by Prof. L. W. King.

— Royal Society. "Antiseptic Action of Substances of the Chloramine Group," by J. B. Cohen, H. D. Dakin, M. Daufresne, and J. Kenyon. "Structure of the Dicyonodont Skull," by I. J. B. and W. J. Sollas. "Analyses of Agricultural Yield—Part III, The Influence of Natural Environmental Factors upon the Yield of Egyptian Cotton," by W. L. Balls. "Function of Chlorophyll, Carotin, and Xanthophyll," by A. J. Ewart.

— Chemical, 8. "The Acid-Gelatin Equilibrium," by H. R. Procter and I. A. Wilson. "Chloro- and Bromotriethylphosphinoacetaldehyde," by W. Caldwell.

FRIDAY, 3rd.—Royal Institution, 5.30. "Corona and other Forms of Electric Discharge," by Prof. S. P. Thompson.

SATURDAY, 4th.—Royal Institution, 3. "Eminent Generals of the last Great War—Wellington's Divisional Commanders," by Hon. J. W. Fortescue.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2936.

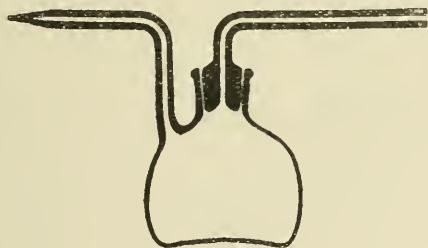
THE DENSITY OF LEAD FROM RADIO-ACTIVE MINERALS.

By THEODORE W. RICHARDS and
CHARLES WADSWORTH.

THE startling differences observed by several investigators (Note 1) in the atomic weight of lead from radio-active sources obviously suggest that other properties also may vary in different specimens, and the comparison of these may be of service in tracing the true causes of the differences in atomic weight. The phenomena are of interest whether or not one accepts the plausible hypothesis of Soddy and Fajans concerning the "isotopes." In a new field of this sort of course as great a variety of facts as possible is peculiarly important.

The present paper details one of a number of lines of research in this direction which are in progress in the Wolcott Gibbs Memorial Laboratory of Harvard University, with the idea of finding out more about the substance admixed with ordinary lead in radio-active minerals, a substance so like ordinary lead that the usual modes of purification do not separate it, and that it produces no change in the ultra-violet spectrum.

The first among the properties to be studied was density (Note 2). The densities of the elements have assumed peculiar interest ever since Mendeléeff and Lothar Meyer, in 1869, showed this property to be a periodic function of



the atomic weight. If the various isotopes have, as would be expected from the atomic volume curve, nearly if not quite the same atomic volume, then of course the isotope with less atomic weight should have less density. The matter was therefore inevitably approached with a preconceived opinion, but during the experimental work the investigators tried to make themselves as independent as possible of any preconceived notions. Preliminary experiments gave evidence that a difference in density really exists; hence the matter seemed worthy of the more careful experiments detailed below.

(Note 1.—Richards and Lambert, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 819; Hönigschmid and St. Horowitz, *Comptes Rendus*, 1914, clviii., 1798; M. Curie, *Comptes Rendus*, 1914, clviii., 1676; Soddy and Hyman, *Journ. Chem. Soc.*, 1914, cv., 1402; also especially, Hönigschmid, *Sitzb. k. Akad. Wiss. Wien.*, cxiii., 11a., December, 1914).

(Note 2.—The density of lead from thorianite has already been studied by Soddy and discussed by Lindemann respectively, *Nature*, 1915, xciv., 615, and xcv., 7. Prof. F. W. Clarke has kindly called our attention to the desirability of studying also several other properties).

Apparatus.

Among the various forms of pycnometer available for determining the density, a form was chosen which for many years has been in use in Harvard, having been designed by one of us in 1898. No adequate description of this apparatus has ever been given, however; hence a brief account of it is now in place. It consists in principle simply of an Ostwald-Sprengel pycnometer, modified for use with solids by the introduction of a glass stopper, as indicated in the diagram, and has the ease of adjustment familiar to those who have used the Ostwald form. Several details concerning it should be mentioned. In the first place the stopper should not be too nearly cylindrical. In a stopper 8 mm. high the upper diameter should be 8 mm. and the lower 7. With this angle the stopper attains on successive settings almost precisely the same point, but is not so conical as to fall out easily. When the joint is very thoroughly ground it is sufficiently watertight for long periods even without a lubricant, but certainty of closure is increased by spreading about 0.5 mgrm. of a lubricant (such as a mixture of hard and soft paraffin and melted rubber) upon the ground joint. This precaution was adopted in the present research.

For the best results the pycnometer should of course be but little larger than the bulk of the substance to be studied, and the internal diameter of its tubes should not exceed 1 mm. Both of these specifications have been recently unheeded by a German firm which has advertised it.

To determine its volume the instrument was filled either with hot water or else in an evacuated apparatus with cold previously boiled water. The two methods gave identical results. It was then left for a long time in an accurately adjusted thermostat kept at 19.94°.

Before weighing the pycnometer was always wiped with a clean, lint-free cloth and was weighed in a balance case containing no drying agent. Twenty minutes in the balance case sufficed amply for the attainment of constant weight, which did not change on standing twenty minutes more.

The following readings of the weight of water contained in the pycnometer—two settings and weighings for each of three adjustments of the stopper—show how accurately the instrument serves its purpose.

TABLE I.—Weights of Water Reduced to Vacuum Standard. Temperature 19.94°.

5.7264	5.7264	5.7264
5.7264	5.7263	5.7264

Five of these six weighings were identical and the other differed only by 0.1 mgrm.

The pycnometer was used with the lead in the same way as with water alone. After drying in an air-bath a thin coating of the lubricant was smeared upon the ground glass stopper. A carefully weighed quantity of lead, prepared in a manner to be described later, was introduced after weighing the pycnometer with its lubricant, and in the first series of experiments (called "1st method" in Table II.) the vessel was filled through the pointed jet with pure hot water, which if previously boiled was found to be without action on the lead. The pycnometer was then placed in the water of a clean thermostat carefully regulated to within one-hundredth of a degree and allowed to come to thermal equilibrium. After the setting of the meniscus the pycnometer was removed and carefully dried and reweighed, just as it had been when containing water alone. In the experiments designated "2nd method" in Table II. the filling was conducted with cold boiled water in a vacuum, according to the method used by Kahlbaum and others (*Zeit. Anorg. Chem.*, 1901, xxix., 237). This is by far the more trustworthy method with a porous substance, but it will be seen that in the present simple case the two methods gave essentially identical results.

TABLE II.—Density of Common Lead. (Temperature 19.94°).

Method.	Sample.	Observed weight of lead.	Weight of lead in vacuo (W).	Observed weight water not displaced.	Corresponding volume.	Volume of pycnometer.	Volume (V) of water displaced.	Density, W/V.
1st.	A	11.3274	11.3270	4.7236	4.7369	5.7364	0.9995	11.333
	A	5.7889	5.7887	5.2111	5.2258	5.7364	0.5106	11.337
	A	5.5202	5.5200	5.2348	5.2496	5.7364	0.4868	11.339
2nd.	A	7.3297	7.3294	5.0758	5.0901	5.7364	0.6463	11.341
	B	15.9150	15.9144	4.3205	4.3327	5.7364	1.4037	11.337
Average								11.337

TABLE III.—Density of Radio-active Lead. (Temperature 19.94°).

Purified by Five Re-crystallisations of Nitrate.

1st.	C	13.5713	13.5708	4.5217	4.5345	5.7364	1.2019	11.291
	C	8.2967	8.2964	4.9874	5.0014	5.7364	0.7350	11.288
2nd.	C	13.4788	13.4783	4.5294	4.5422	5.7364	1.1943	11.286
	C	7.5013	7.5010	5.0576	5.0719	5.7364	0.6645	11.288
Average								11.288

Further Purified by Five Re-crystallisations as Chloride.

1st.	D	12.9527	12.9522	4.5764	4.5893	5.7364	1.1471	11.291
	D	7.9345	7.9342	5.0196	5.0338	5.7364	0.7026	11.292
2nd.	D	11.5183	11.5179	4.7026	4.7159	5.7364	1.0205	11.287
	D	6.6672	6.6670	5.1312	5.1457	5.7364	0.5907	11.287
Average								11.289

Hence the results are as follows :—

Density of ordinary lead	11.337
Density of radio-active lead from nitrate	11.288
Density of radio-active lead from chloride	11.289

Preparation of Materials.

The best method of purifying lead salts is by crystallisation of the nitrate (Baxter and Grover, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 5). A large quantity of lead from radio-active sources (obtained through the kindness of Mr. S. Radcliff and Mr. E. R. Bubb, of the Radium Hill Company of Australia) was dissolved in nitric acid and the nitrate was recrystallised five times by dissolving the crystals in hot water and adding a large excess of nitric acid. In this way the crystals separated from a large volume of mother liquor, and the purification was very rapid. The pure nitrate was then divided into several portions, of which one was immediately afterward electrolysed in quartz vessels from hot solution, using electrodes of platinum wire. This procedure gives a very beautiful crystalline deposit, which is easier to wash and for this reason purer than the somewhat spongy deposits obtained from cold solution. The subsequent treatment of these crystals will be described later. (Sample C).

Another portion of the pure lead nitrate was precipitated as chloride by pure hot hydrochloric acid, obtained by distilling pure acid of constant boiling-point. The precipitate was thoroughly washed and recrystallised as chloride four times. This chloride was then electrolysed, using a fine-grained porous cup to surround the anode in hot, slightly acid solution, and the crystals of lead thus obtained were thoroughly washed and treated like the preceding. (Sample D).

Finally samples of ordinary lead chloride, which had been carefully purified by Dr. J. W. Shipley, were treated in the same way. This lead chloride had been twice recrystallised after precipitation from a solution of the acetate which had itself been several times recrystallised. The electrolytic crystals of pure ordinary lead were thoroughly washed and treated like the radio-active metal. Two such preparations were made and designated A and B.

Each of these samples of clean lead crystals was finally fused in a mould of pure sugar charcoal made for the purpose. This mould or boat had been made from a paste of

powdered sugar charcoal, sugar, and water, packed into an "alundum" boat, moulded into the desired shape, heated cautiously in an air bath, and when dry thoroughly ignited before the lead was placed upon it. Upon the hard, smooth surface of this charcoal boat each bar of lead was melted, the boat having been placed in a hard glass tube, in a current of pure, dry hydrogen. This in turn was made from the electrolysis of sodium hydroxide, containing some baryta, passed over red-hot copper, and finally dried by potassium hydroxide, previously fused with a little permanganate. The resulting bars of lead were beautifully bright and clean. After cooling each was removed, carefully freed from adhering carbon, cut into small pieces, and hammered on a polished anvil with a clean steel hammer. Finally these hammered bars were scrubbed with clean sea-sand, dried and polished with a clean cloth, and placed in a desiccator over fused potash. Each of the three samples was subjected to precisely the same treatment, so that no difference in density could arise from any difference in the preparation of the metal.

With each of these varieties at least four determinations of the density were made, using different amounts of material, so as to be sure that no systematic error existed in the method. The data are given below in full, the weighings both in air and corrected to vacuum being recorded. It will be remembered that the weight of water contained by this pycnometer was 5.7264 grms. in vacuum, the average amount in air being 5.7203. The temperature was in every case 19.94°.

Evidently the density of the lead from radio-active sources is 0.049—that is to say, 0.43 per cent lower than that of ordinary lead, a very striking difference, in the sense which was expected.

Before considering these results further, the results of others on the density of ordinary lead may receive a moment's consideration. As usual these are highly conflicting, for the determination of the density of solids has been highly uncertain; good results are rare. Earlier values for the density of lead have varied from 11.19 to 11.37 (see, for example, Kahlbaum and others, *Zeit. Anorg. Chem.*,

1901, xxix., 278). The most accurate of these seems to have been that of Kahlbaum, Roth, and Siedler, who, however, used only distillation as a means of purifying their metal. Their values were 11·341 and 11·347 for unpressed and pressed lead respectively (*Zeit. Anorg. Chem.*, 1901, xxix., 280). As they themselves showed that the common metallic impurities in lead were easily volatile under the conditions which they employed, and therefore might have contaminated their distillate, their result, although good, cannot be deemed certainly accurate. The qualitative experiment in which they distilled a ten-pfenning piece is hardly convincing as evidence of precision (*loc. cit.*, 195). Of course these criticisms do not apply to their interesting conclusions about the effect of pressure, except in so far as possible impurities might affect the crystalline habit of the solid metal, and perhaps cause small vacant spaces in the structure.

The difference between the result of Kahlbaum and his collaborators (11·341) and our result (11·337) for ordinary lead is only 0·004 or 0·04 per cent. As density determinations go this is a good agreement. The only impurities likely to have been in our sample are hydrogen and carbon, which might possibly cause a deviation of this magnitude, although we have no definite evidence that either of these elements is soluble in melted lead to an appreciable extent. Another possible cause of difference lies in a conceivable allotropy in the metal (Cohen and Inouye, *Chem. Weekblad.*, 1910, 1).

Whatever may be cause of this slight difference it does not affect the arguments to be drawn from our comparative results, for each of our samples of metal was treated precisely in the same way. Hence each sample of lead must have been equally saturated with carbon and hydrogen if any dissolved, and each must have been of the same modification. It will be noted that the greatest deviation from the mean is 0·004 in the case of the common lead and only 0·003 in the case of each sample of radio-active lead. The difference, on the other hand, between ordinary lead and the mean of the two samples of radio-active lead is, as has been said, 0·049, over twelve times the greatest deviation from the mean and over twelve times the difference between our pure lead and that of Kahlbaum and his collaborators. There can be no question, therefore, that these results show a real difference between the two kinds of lead, which must be referred to the admixture causing the low atomic weight of radio-active lead.

Furthermore it should be noted that the five additional recrystallisations of the second radio-active sample (D) as chloride produced no essential change in the purity of the lead, as indicated by its density; hence it is clear that more drastic means than recrystallisation must be taken to separate the modifications.

It is interesting to compare these results with those of Soddy, who found in lead from thorite slightly higher density than that of ordinary lead, just the opposite to the phenomenon described in this paper (*loc. cit.*). Soddy earlier found in lead from thorite (presumably a similar sample) also an atomic weight higher than that of ordinary lead, whereas the atomic weight of our Australian radio-active lead has been found, in experiments not yet published, to be much lower than that of ordinary lead, namely 206·3 instead of 207·2. Hence Soddy's results are not inconsistent with ours; they seem rather to indicate that a different admixture was present in his material.

Returning to our results, it is interesting to note that the atomic volume of the Australian radio-active lead is very nearly the same as that of ordinary lead, because $206·3/11·288 = 18·276$, whereas for ordinary lead $207·2/11·337 = 18·277$. The difference between these values for the atomic volume is so small as to be no greater than the probable limit of error of the experiment; hence it is clear that the atomic volume of radio-active lead is essentially equal to that of ordinary lead.

Of course no one knows as yet what proportion of im-

purity exists in this radio active sample, which doubtless contains some ordinary lead. If the true atomic weight of the pure isotope is really 206, this sample must have consisted chiefly of the isotope, and the atomic volume of the pure isotope must be very nearly 18·3. On the other hand it is possible that the theory is incomplete, and that the lowering of atomic weight and density is due to the admixture of a much smaller amount of a substance with much lower atomic weight. In that case the atomic volume of the admixture is of course less certain, but it probably is near 18.

It is a pleasure to express our indebtedness to the Carnegie Institution of Washington for generous pecuniary support in this investigation.

Summary.

The density of ordinary lead (having an atomic weight of 207·2) and of lead from Australian radio-active sources (having an atomic weight of 206·3) was carefully determined in a convenient pycnometer, which is described in detail for the first time although long in use. The density of ordinary lead reduced to the vacuum standard was found to be 11·337 and that of radio-active lead 11·288. Continued fractionation produced no change in this low density, and it could not have been due to any irregularity in preparing the metal, since the samples were all prepared in the same way. This difference in density is especially interesting, because it almost exactly parallels the difference in atomic weight; thus the atomic volume of radio-active lead is found to be almost exactly equal to that of ordinary lead, the figures being each very nearly 18·28.—*Journal of the American Chemical Society*, xxxviii, No. 2.

ON SIMPLE AND MIXED ALKYL PHOSPHATES.

By W. A. DRUSHEL.

WHEN a sodium alcoholate free from the alcohol is treated with the theoretical amount of phosphorus oxychloride at room temperature in the presence of ether a good yield of the corresponding trialkyl phosphate is obtained (Limpricht, *Ann. Chem. Pharm.*, cxxiv., 347). By means of this reaction Lossen and Köhler (*Ann. Chem. Pharm.*, cclxii., 209) in 1891 prepared trimethyl phosphate, triethyl phosphate, and from these esters they prepared by a method to be described the mixed esters, dimethyl-ethyl phosphate and methyl-diethyl phosphate. They studied these simple and mixed alkyl phosphates with special reference to their behaviour toward barium hydroxide at room temperature. From their observations they drew the following conclusions:—

1. That the esters of phosphoric acid are far more stable than the esters of organic acids toward aqueous barium hydroxide.
2. That the salts of dialkyl phosphoric acids are much more stable than the trialkyl phosphates.
3. That more than one alkyl group of a trialkyl phosphate may be hydrolysed off only with the greatest difficulty, if at all.
4. That the decomposition of mixed alkyl phosphates by aqueous barium hydroxide proceeds in an unusual manner, in that in mixed alkyl phosphates one alkyl group is hydrolysed off to the exclusion of the other. Apparently the same methyl-ethyl-barium phosphate was obtained by these investigators by the action of barium hydroxide upon both methyl-diethyl phosphate and dimethyl-ethyl phosphate.

The purpose of the present investigation was to prepare a larger number of the simple and mixed esters of orthophosphoric acid, to study their properties and rates of hydrolysis in decinormal hydrochloric acid, and to examine the validity of Lossen and Köhler's fourth conclusion since this conclusion is contrary to the rule observed in the case of esters of dibasic and polybasic

organic acids. In general, the methods described by Lossen and Köhler were used in the preparation of the esters prepared and studied in this investigation. For the preparation of the simple esters sodium alcoholate in each case was prepared by dissolving a weighed amount of pure metallic sodium in a sufficient excess of the desired alcohol. After the sodium was completely used up the excess of alcohol was distilled off in an oil-bath, heating the bath finally at 180° as long as any alcohol distilled over. The residue of sodium alcoholate was cooled, covered with absolute ether, and treated with the theoretical amount of phosphorus oxychloride, diluted with an equal volume of absolute ether, by adding the diluted phosphorus oxychloride in small portions through a reflux condenser, taking care to keep the reaction mixture cool by immersing the flask in cold water. At the conclusion of the reaction the residue of sodium chloride was filtered off, the filtrate distilled on a warm water-bath to remove the ether, and the residue subjected to fractional distillation. The fractionation was made at diminished pressure for all of the esters except trimethyl phosphate, triethyl phosphate, and dimethyl-ethyl phosphate. These three esters were distilled at ordinary pressure without decomposition.

The mixed alkyl phosphates were prepared from the simple esters by making successively the barium salts by the action of aqueous barium hydroxide upon the simple esters at room temperature, the free dialkyl phosphoric acids by the action of sulphuric acid upon the purified barium salts, the silver salts of the dialkyl phosphoric acids by the neutralisation of these acids with silver oxide, and finally the mixed alkyl phosphates from the silver salts by the action of the appropriate alkyl iodides in ethereal solution. The silver iodide was then filtered off, the ether distilled off from the filtrate, and the residue fractionally distilled, generally under diminished pressure. The boiling-points of these simple and mixed esters at diminished or ordinary pressure, their densities at 0° and at room temperature, and their solubilities in water at room temperature were determined, and are recorded in Table I. According to Winssinger's observation the tripropyl phosphate decomposes when boiled even *in vacuo* (*Bull. Soc. Chim.*, xlviii., 111). In order to test the correctness of this observation this ester was re-distilled four times at a pressure of 15 mm. without any change in the boiling-point observed in the first distillation, and without any other evidence of the decomposition of the ester. The isobutyl ester was likewise re-distilled at 15 mm. without any evidence of decomposition.

TABLE I.

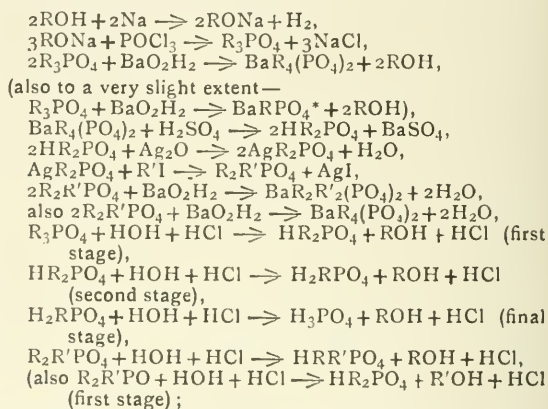
Esters.	Boiling point.	Pressure in mm.	Density—		Solubility in water at 25°.
			0°.	22°.	
Me ₃ PO ₄ (a)	197	760	1·218	1·200	1 : 1
Et ₃ PO ₄ ..	215	760	1·071	1·056	1 : 1
Pr ₃ PO ₄ ..	131	15	1·025	1·007	1 : 155
Isobu ₃ PO ₄ ..	152	15	0·978	0·965	1 : over 1000
Me ₂ EtPO ₄ ..	203	760	1·176	1·161	1 : 1
Me ₂ PrPO ₄ ..	116	15	1·195	1·180	1 : 1
MePr ₂ PO ₄ ..	129	20	1·077	1·059	1 : 22
Et ₂ PrPO ₄ ..	130	20	1·098	1·077	1 : 1
EtPr ₂ PO ₄ ..	145	20	1·046	1·025	1 : 45

(a) Me denotes methyl; Et, ethyl, &c.

In order to determine whether one alkyl group in mixed alkyl phosphates is hydrolysed to the exclusion of the other alkyl group contrary to the rule in the case of esters of organic acid, the barium salts of a number of simple and mixed alkyl phosphates were prepared by the action of a slight excess of barium hydroxide upon the esters in aqueous solution either at room temperature or upon the steam-bath, were purified and analysed for barium, obtaining the results recorded in Table II. It is to be observed that when barium hydroxide reacts with simple alkyl phosphates the barium content of the resulting salts agrees well with the calculated amount, and that when

barium hydroxide under the same conditions acts upon mixed alkyl phosphates in no case does the amount of barium found in the resulting salts agree with the amount calculated for the theory that only one of the two different alkyl groups is hydrolysed off to the exclusion of the other. It is safe to conclude, contrary to Lossen and Köhler's theory, that in mixed alkyl phosphates barium hydroxide does not remove one of the different alkyl groups to the exclusion of the other, and that, although one alkyl group may be more readily attacked than the other of two different alkyl groups, the reaction does not by any means go wholly in that direction.

The reactions involved in the preparation and hydrolysis of alkyl phosphates may be briefly summed up in the following equations, where R denotes an alkyl group and R' a different alkyl group :—



similarly for the second and final stages. In each case the first alkyl group is hydrolysed off more easily than the second and third groups, which is in agreement with Lossen and Köhler's observation for the saponification of these esters by barium hydroxide at room temperature.

TABLE II.—Barium Salts of Dialkyl Phosphoric Acids Prepared and Analysed for Barium.

Esters and salts.		Per cent of barium.	
		Found.	Theory.
Ba(Me ₂ PO ₄) ₂		35·2	35·4
Ba(Et ₂ PO ₄) ₂	r	35·3	31·2
Ba(MeEtPO ₄) ₂	rI.	31·3	34·0
from	r	34·0	33·0 (a)
MeEtPO ₄	rII.	34·1	34·1
Ba(MePrPO ₄) ₂	rI.	34·1	34·5 (b)
from	rII.	32·0	30·6 (a)
Me ₂ PrPO ₄	s	32·1	32·1
from	sI.	34·1	27·5 (c)
MePr ₂ PO ₄	sII.	28·8	28·9 (d)
Ba(EtPrPO ₄) ₂	s	28·9	31·6
from		31·6	29·1 (e)
Et ₂ PrPO ₄		31·5	
from	r	27·7	27·7 (f)
EtPr ₂ PO ₄		27·7	

(a) Salt probably contained some BaMe₄(PO₄)₂.

(b) Calculated for BaMe₄(PO₄)₂.

(c) Calculated for BaPr₄(PO₄)₂.

(d) Salt probably contained some BaPr₄(PO₄)₂.

(e) Salt probably contained some BaEt₄(PO₄)₂.

(f) Probably chiefly BaPr₄(PO₄)₂ formed.

r, Saponification was made at room temperature; s, on the steam-bath.

* This salt being insoluble is readily removed by filtration.

The acid hydrolysis of the esters recorded in Table III. was made in flasks contained in a boiling water-bath especially constructed for the purpose, and fitted with a reflux condenser. Decinormal hydrochloric acid was used as the hydrolytic agent, and the course of the reaction was followed in the usual way by making titrations with decinormal barium hydroxide, using phenolphthalein as an indicator. In each case weighed amounts of ester were used, making the concentration of ester in the reaction mixture initially decinormal. Since the end-point of the primary hydrolysis stage could not be determined by titration on account of the interference of the secondary and tertiary stages, it was calculated in each case from the weight of ester taken. However, since the secondary and tertiary hydrolysis products form insoluble barium salts, it was possible to observe directly how far the titrations furnished reliable data for calculating the velocity constants for the primary hydrolysis stage. The constants recorded in Table III. represent only the primary hydrolysis stage, the latter constants in some cases being perhaps slightly influenced by the secondary reaction. In calculating the constants the reaction was considered of the first order, and no account was taken of the possible hydrolytic effect of the very weak dialkyl phosphoric acids set free in the primary hydrolysis stage. The acid hydrolysis was first attempted at 25°, but was found to proceed so slowly as to make it impracticable at this temperature. A fifth normal solution of trimethyl phosphate in decinormal hydrochloric acid was allowed to stand for thirty-two days at 22° to 25° with an increase of only 5 per cent in the total acidity of the reaction mixture, and the triethyl ester hydrolyses only about one-fourth as fast. The measurements were therefore made at 100°.

TABLE III.—Hydrolysis of Alkyl Phosphates in N/10 HCl at 100°.

Me ₃ PO ₄ , 600 min. 10° K.	Et ₃ PO ₄ , 2100 min. 10° K.	Me ₂ EtPO ₄ , 830 min. 10° K.	Me ₂ PrPO ₄ , 700 min. 10° K.	Et ₂ PrPO ₄ —	
				I. 1770 min. 10° K.	II. 760 min. 10° K.
209	50.9	182	203	62.1	63.9
215	51.8	184	209	59.2	61.5
224	50.1	189	207	61.1	59.5
223	55.3	183	200	61.6	61.2
225	55.2	184	199	62.1	
	55.4	189	198	61.9	
219	53.7	185	202	61.3	60.8

In this table the ranges of time in minutes through which the titrations were used in the calculation of the constants are given at the top of the columns. In this table of constants the very marked difference in the resistance to hydrolysis of the three alkyl groups, methyl, ethyl, and propyl, is noteworthy. The distinct effect of the single alkyl group in the mixed esters upon the rate of hydrolysis is also to be observed. According to Lossen and Köhler's theory, in mixed alkyl phosphates the alkyl group occurring twice is saponified to the exclusion of the single alkyl group. In order to explain the velocity constants for the mixed esters on this theory it would be necessary to assume that the presence of the single alkyl group increases the resistance to hydrolysis of the alkyl group occurring twice in the ester. The effect observed is more simply explained by assuming that the hydrolysis is not confined to the alkyl group which occurs twice in the molecule, but that in at least some of the molecules the single alkyl group is hydrolysed off, yielding in the hydrolysis products acids of both types HRR'PO₄ and HR₂PO₄. This view is in agreement with the results obtained in the barium hydroxide saponification shown in Table II.

Conclusions.

1. Both the simple and mixed alkyl phosphates are very stable at room temperature even in decinormal hydrochloric acid, but are rapidly saponified by barium hydroxide.

2. All of the alkyl groups are hydrolysable, although the first group is much more easily attacked than the second and third.

3. In mixed alkyl phosphates the alkyl group which occurs twice is not hydrolysed to the exclusion of the single group, but on the contrary the hydrolysis product contains both types of dialkyl phosphoric acids, HRR'PO₄ and HR₂PO₄, with the first type probably very largely in excess of the second type.

4. Tripropyl phosphate and triisobutyl phosphate are both distillable *in vacuo* without decomposition.—*American Journal of Science*, xl., p. 643.

THE NEED OF A LARGE GOVERNMENT INSTITUTION FOR CHEMICAL RESEARCH.

By C. ALFRED JACOBSON.

THE idea embodied in the present paper was born in Germany in 1912, then rocked in a cradle of the deep, nursed under the shadows of the skyscrapers of New York, and finally reared to maturity on the arid sands of Nevada.

Chemistry is one of the basic sciences. It is the foundation upon which countless industries have been built. All other sciences are dependent upon it to a greater or less degree. In short, chemistry is the corner-stone in the edifice we call civilisation, and it has given a different meaning to the word *Kultur*. It is needless here to dwell upon the value of this branch of science to our industrial and economic life, and even to our existence as an independent nation, for this is apparent even to those who have given the subject but a cursory consideration. There may be those, however, who believe that our present knowledge of chemistry is quite complete, and what we need is a better application of the known rather than to be continually striving to acquire more knowledge. To such let me say that although 200,000 or more definite chemical compounds have been described and thousands of chemical books have been written the known is still infinitesimal compared to the unknown in this field of science. Graphically speaking, if a tennis ball were thrown into Lake Michigan the amount of water wetting the ball compared to the rest of the water in the lake would fairly represent our present chemical knowledge compared to that which is still unknown. Whether these estimates are correct or not matters little. The essential thing is that there are vast riches of knowledge yet uncovered in every field of science, and not the least in chemistry.

Our civilisation will advance just in proportion as we are able to push back the frontier and lay bare the facts of nature, and make them serve our needs. Not until the soldier has had his baptism of fire at the front does he realise or appreciate what war means, and the analogy holds equally well for the scientist. The research men are the ones at the front, and they are in a better position than anyone else to appreciate the economic importance and value of scientific research.

It would seem that no one could read the symposia on the Contributions of the Chemist to American Industries, published in the April and November (1915) issues of the *Journal of Industrial and Engineering Chemistry*, without being profoundly impressed with the fact that chemistry is after all at the basis of nearly all our industries. Products whose values mount into the billions of dollars annually are largely conditioned upon the work of the chemist, and the end is not yet.

This branch of science is not only vital to constructive agencies but even more so to the destructive ones, such as those of the army and navy. The present European war teaches us that men and military training are of far less importance to success than a high development of the science of chemistry, and it behoves us to learn this lesson quickly, lest Belgium's and Russia's fate befall us.

President Wilson's careful interpretation of the signs of the times and of the significance of current developments across the water makes him blow the bugle for preparedness. He is perhaps better able from his exalted position than any other American to peer into the war cloud on the horizon and tell of its foreboding to the country. On the other hand, we could scarcely point to a more ardent supporter of peace on earth and goodwill among men than he. It would be well, therefore, at a time like this to sacrifice political views and prejudices for the one fundamental principle of loyalty to our country.

In the matter of national defence a big step forward has been taken through the creation of the Naval Advisory Board. It is now to be hoped that wise and conservative plans will be made and that the recommendations offered by the Board will receive adequate legislative support. America has gained recognition for the excellence of its chemical work in several different fields, but if we are to compete with Europe and hold a leading place among the nations we must extend this excellence to many more departments, and in order to do that there must be co-ordination of the research work and a more intimate co-operation by the manufacturing and commercial interests of the country. Speaking of this co-operation it should be said that Prof. Charles H. Herty, President of the American Chemical Society, has discussed this subject in a very clear and masterful way in the October issue of the *Journal of the American Chemical Society*, and it would be well for every chemist as well as every "captain of industry" to read his article.

Need for Government Research Institution.

As for co-ordination of chemical research, I would say that after several years of thought upon the subject the following hypothetical plans for a large Government institution for chemical research have gradually been evolved. By an Act of Congress provision should be made for the establishment of an institution for chemical research composed of 50 major departments and 100 minor departments, comprising about 50 buildings, to be located near one of the larger cities of the country. Each of the major departments should be composed of a chief chemist, 4 associate chemists, 8 assistant chemists, 5 laboratory helpers, and 2 stenographers, and each of the minor departments of 1 chief chemist, 2 associate chemists, 4 assistant chemists, 3 laboratory helpers, and 1 stenographer. The total working staff of the institution would then be 150 chief chemists, who should constitute the Administrative Council, 400 associate chemists, and 800 assistant chemists. There would also be 550 laboratory helpers and 200 stenographers, making a total of 2100 persons, exclusive of the force in the adjunct departments. The character and importance of the work should determine whether it would constitute a major or minor department. Certain lines of work might be started as minor departments, and when conditions and results warranted changed to the major form.

The major and minor departments suggested as a preliminary working basis are listed in Table I., the major departments being printed in capitals. In addition to the research departments there should be the following adjunct departments: a department of supplies, a department of glass-blowing, a department of publications, a department of standards (for weights, measures, thermometers, barometers, &c.), a machine shop, and a testing laboratory for chemicals and reagents.

The research departments enumerated may be considered as only tentative suggestions which could be changed and revised by representative committees for that purpose. It is seen that various departments merge into one another and no sharp dividing line can be drawn, but this is true in almost every realm of nature, and it therefore becomes necessary to affix certain arbitrary boundaries.

To get an idea of the approximate initial cost of

founding an institution of this magnitude the estimates in Table II. are given. It is considered that 500 acres of land would suffice, which could perhaps be obtained for 10000 dol., or less, per acre. The 100 minor departments would be housed in twenty-five buildings, making four departments to each building, and twenty-five major department buildings of approximately the same size, each providing for two major departments.

An estimate for the annual running expenses of the institution at maximum salaries is also given in Table II.

No doubt many of the details of the organisation and sources of expense would be encountered that have not been included in this brief summary, but, as mentioned before, it is intended only as a basis for something tangible along a more hopeful and promising line of national progress.

The greatest difficulty will be in filling the various research positions, but this would not necessarily have to be done immediately. A good live nucleus would soon build an efficient working force round itself, and an institution of such gigantic proportions would inevitably stimulate research in every other institution in the country, and be a source of unprecedented national development for peace as well as for war.

It would be the brain of the chemical nervous system of our body politic, and would co-ordinate the widely scattered chemical research ganglia. This could be accomplished at an annual cost of less than one-half the cost of a modern battle cruiser. There would be no popular or political influences brought to bear upon such an organisation, and the sole qualification for every member of the staff would be merit.

The institution would not only discover principles and things in nature, but it would discover men—men whose power would set the elements in commotion, and cause accepted theories to tremble upon their foundations, but who without such opportunities might never produce a ripple on the placid stream of public consciousness. Each member would have the advantage of expert counsel in practically every other field of chemistry, and the close association and interrelationship of departments would have a stimulating effect upon the personnel and work of the entire organisation.

Efficiency and economy could be secured in ways which are impossible of attainment in smaller and widely separated institutions.

No systematic research work is now being carried on in this country in the larger number of the departments here enumerated, although every one of them offers a fertile field for investigation. One could not determine in advance which department is likely to yield the most important results. The biggest surprises are likely to come from directions least expected.

One entirely new field for investigation has been suggested, namely, odour chemistry. Since odour particles are so characteristic it would seem possible to study their penetrability through media, their absorptive or adhesive properties, their deflectibility in electromagnetic and electrostatic fields of force, as well as the influence exerted upon them by temperature. Odourless compounds may send out characteristic odour particles that are beyond the range of the olfactory nerve even as there are ether waves beyond the range of the optic nerve and sound waves beyond the auditory nerve. A more rapid system of qualitative analysis might be worked out along this line.

While working upon certain extracts of water hemlock the author has made several startling observations. In drying a small portion of one of these products in a desiccator it suddenly exploded with such violence that the 9-inch Hempel desiccator was blown to dust. Another product from the same plant was found to ignite spontaneously in the air at a slightly elevated temperature, and who is able to say whether these or similar discoveries might not result in commercially valuable products if they could be followed up with that end in view?

TABLE I.—Research Department Suggested for Government Research Institution.

No.	Department.	No.	Department.
1.	IRON AND STEEL.	77.	Tannins and Tanning Materials.
2.	Copper.	78.	Animal Fats.
3.	Lead.	79.	FISH OILS AND FISH PRODUCTS.
4.	Mercury and amalgams.	80.	RUBBER.
5.	METALLIC ALLOYS.	81.	SYNTHETIC RUBBER.
6.	Metallic Vapours.	82.	Synthetic Leather.
7.	Rare elements.	83.	Synthetic Dielectrics.
8.	Radio-active Elements and Minerals.	84.	Uric Acid Derivatives.
9.	Inorganic Acids.	85.	Camphor and Synthetic Camphor.
10.	Inorganic Salts.	86.	ENZYMES.
11.	METAL PRESERVATION.	87.	Antibodies.
12.	METALLURGY.	88.	Bacterial Chemistry.
13.	Metal Plating.	89.	Blood and Lymph.
14.	STORAGE BATTERIES AND DRY CELLS.	90.	Normal and Pathogenic Sera.
15.	SILICATES.	91.	ANIMAL SECRETIONS.
16.	GLASS AND QUARTZ GLASS.	92.	Vegetable Exudates.
17.	INORGANIC COLLOIDS.	93.	Antiseptics and Disinfectants.
18.	ORGANIC COLLOIDS	94.	Anæsthetics.
19.	CARBON AND CARBIDES.	95.	MEDICINAL PLANTS.
20.	ORGANO-METALLIC DERIVATIVES.	96.	Toxicology.
21.	CLAY AND CERAMICS.	97.	Dairy Products.
22.	PORCELAIN & GLAZING MATERIALS.	98.	Legumes and Grasses.
23.	Aliphatic Hydrocarbons.	99.	PETROLEUM.
24.	BENZENE AND CYCLIC HYDROCARBONS.	100.	COAL TAR.
25.	PHENOL DERIVATIVES.	101.	Mordants.
26.	ANILINE DERIVATIVES.	102.	EXPLOSIVES.
27.	TERPENES.	103.	GASES.
28.	Alcohols.	104.	Celluloid and Synthetic Ivory.
29.	Aldehydes and Ketones.	105.	FIXATION OF ATMOSPHERIC NITROGEN.
30.	Unsaturated Aldehydes.	106.	Paints.
31.	Organic Acids.	107.	Stains and Preservatives.
32.	Cyanogen Derivatives.	108.	Corn, Sorghum, and Sugar-beet Products.
33.	ANTHRACENE DERIVATIVES.	109.	Grain, Rice, and Potato Products.
34.	QUINOLINE DERIVATIVES.	110.	Seeds and Seed Germination.
35.	ALIZARINE DERIVATIVES.	111.	Hemp, Flax, and Cordage Materials.
36.	Indigo Derivatives.	112.	Paper.
37.	PYRIDINE AND HETEROCYCLIC COMPOUNDS.	113.	Marine Vegetable Products.
38.	Pyrone Derivatives.	114.	Marine Animal Products.
39.	DIAZO COMPOUNDS.	115.	Forest Products.
40.	Monoses and Dioses (Sugars).	116.	Fruit Products.
41.	Polyoses (Sugars).	117.	Desert Plant Products.
42.	GLUCOSIDES.	118.	TROPICAL PLANT PRODUCTS.
43.	Starches, Dextrines, and Complex Carbohydrates.	119.	Silk and Silk By-products.
44.	Cycloses.	120.	Packing House By-products.
45.	Pectines.	121.	Sewage Utilisation.
46.	CELLULOSE DERIVATIVES.	122.	Fuels and Smoke Abatement.
47.	Stearines.	123.	Cements and Building Materials.
48.	Nitrogenous Glucosides.	124.	Asbestos and Mica Products.
49.	Bitter Principles.	125.	AERONAUTIC MATERIALS.
50.	Vegetable Mucilages.	126.	Fire Extinguishers.
51.	Lichen Substances.	127.	Animal Metabolism.
52.	Saponines.	128.	Catalysis.
53.	Gums and Resins.		
54.	Waxes.		
55.	SOAPS AND ETHEREAL SALTS.		

TABLE I. (continued).

No.	Department.	No.	Department.
56.	PURINE AND PYRIMIDINE BASES.	129.	Dental Supply Products.
57.	Nucleo-Proteids and Nucleic Acids.	130.	CHEMICAL CRYSTALLOGRAPHY.
58.	Biliary Substances and Pigments.	131.	Photographic Materials.
59.	Humins and Humic Acids.	132.	Photographic Reproduction.
60.	ESSENTIAL OILS.	133.	Colour Reproduction.
61.	VEGETABLE OILS (DRYING).	134.	Chemical Dynamics and Equilibrium.
62.	VEGETABLE OILS (NON DRYING).	135.	Electrochemistry.
63.	Varnishes and Wood Preservatives.	136.	Electrical Conductivity.
64.	Organic Sulphur Derivatives.	137.	Thermochemistry.
65.	Lipoids and Phosphatides.	138.	Odour Chemistry.
66.	VEGETABLE PROTEINS.	139.	Low Temperature Chemistry.
67.	ANIMAL PROTEINS.	140.	High Temperature Chemistry.
68.	POLYPEPTIDES.	141.	Water, Hydrates, and Hydration.
69.	AMINES & AMINO ACIDS.	142.	Solubilities.
70.	Albuminoids.	143.	Molecular Weights.
71.	Organic Halides.	144.	Spectral Chemistry.
72.	Chlorophylls.	145.	Infra-red and Ultra-violet Photography.
73.	Vegetable Colouring Matters.	146.	Plant Metabolism.
74.	Animal Colouring Matters.	147.	FOODS.
75.	VEGETABLE ALKALOIDS.	148.	DRUGS AND PHARMACEUTICAL MATERIALS.
76.	Animal Poisons and Venoms.	149.	Sanitation and Disease Prevention.
		150.	Atomic Morphology and Atomic Weights.

TABLE II.—Initial Cost of Founding Institution.

	Rate.	Total.
	Dols.	Dols.
Cost of land	—	500,000
Cost of 50 buildings.. .. .	350,000	17,500,000
Equipment of 50 buildings	150,000	7,500,000
Buildings and equipment for adjunct departments.. .. .	—	1,500,000
Cost of departmental libraries	—	1,000,000
		27,500,000

Department Salaries.

	Rate.	Major.	Minor.
		No. Total.	No. Total.
Chief chemists	—	1 6,000	1 5,000
Associate chemists	2,500	4 10,000	2 5,000
Assistant „	1,500	8 12,000	4 6,000
Laboratory helpers	900	5 4,500	3 2,700
Stenographers	1,200	2 2,400	1 1,200
Total per department per year		34,900	19,900

Summary of Annual Expenses of Institution.

Salaries—			
Director (elected by the Council)	10,000		
50 major departments at 34,900 dols.	1,745,000		
100 minor departments at 19,900 dols.	1,990,000		
50 glass-blowers at 1200 dols.	60,000		
100 other employees at 1200 dols.	120,000		
Supplies and Incidentals—			
50 major departments at 15,000 dols.	750,000		
100 minor departments at 8000 dols.	800,000		
Miscellaneous expenditure	200,000		
Total annual expenses	5,675,000		

Even if a smaller institution than the one here proposed were founded it would doubtless serve a very useful end, and in the course of time develop along the more important lines. It is not improbable that the industrial concerns would recognise the value of such co-ordination, and would endow certain departments of the institution through which they would be directly benefited.

Enough has been said to start the refrain if the idea possesses some intrinsic value. This lump of earth, after being sifted through the press and cupelled by our leading chemists, might leave a residue which, when alloyed with the proper elements and then passed through the legislative machines, might produce a filament that will glow and sparkle when a current of American energy and patriotism is passed through it, shedding light into all the world.—*Journal of Industrial and Engineering Chemistry*, viii., No. 1.

THE

DETERMINATION OF ALKALINITY IN WATER.

By F. W. BRUCKMILLER.

FOR the determination of alkalinity in waters the Standard Methods of Water Analysis recommends that a suitable portion of the water (usually 50 cc.) be titrated with 0.02 N sulphuric acid using phenolphthalein, and that a like portion be titrated with erythrosine of methyl-orange. The results of each titration are expressed in p.p.m. of CaCO_3 , and by means of the following table the alkalinity due to carbonates, hydrates, or bicarbonates is determined.

Table showing Relation between Alkalinity by Phenolphthalein and that by Erythrosine in presence of Bicarbonates, Carbonates, and Hydrates.

	Bicarbonates.	Carbonates.	Hydrates.
P = O	E	O	O
P $\frac{1}{2}$ E	E-2P	2P	O
P = $\frac{1}{2}$ E	O	2P	O
P $\frac{1}{2}$ E	O	2(E-P)	2P-E
P = E	O	O	E

E = Erythrosine alkalinity.

P = Phenolphthalein alkalinity.

For practical routine work this method is not very well suited. Too much time is unnecessarily consumed in measuring out two separate portions of a water to determine its alkalinity, when the same results can be obtained by the use of only one. Furthermore, if both titrations are carried on in the same sample, the interpretation of the results are made a trifle confusing if one tries to use the above table. Because of these facts, the method given below, as well as the interpretation of the results, have been used exclusively by the Water and Sewage Laboratory, University of Kansas, and have been found to be quite satisfactory. We have been unable to find published elsewhere a similar statement of the procedure as we employ it. The subject matter it contains is not new, nor original with us. Cameron first showed that carbonates could be titrated in the presence of bicarbonates (*Am. Chem. Journ.*, 1900, xxiii., 481), while Hehner was the first to show that methyl-orange could be used for the determination of bicarbonates (*Analyst*, viii., 77). We have simply written down a long used procedure in a clear manner with the hope that it will prove of value to those who are now employed in water work as well as to those who will in the future take up such work.

Procedure Using Methyl-orange.

To 50 cc. (or to 100 cc. if the alkalinity is low) of the water to be tested in a white porcelain casserole, or in an Erlenmeyer flask held over a white surface, add 4 drops of

phenolphthalein indicator (1 grm. in 1 litre of 95 per cent alcohol). If the solution turns red, hydroxides or normal carbonates are indicated. Proceed then as in (a). If no change in colour appears, proceed as in (b).

(a) Add N/50 sulphuric acid from a burette until the solution becomes colourless. Record the number of cc. used, and call phenolphthalein titration.

Now add 2 drops of methyl-orange (0.5 grm. in 1 litre of water) indicator, and add N/50 sulphuric acid until a faint pink occurs. Record the number of cc. used, and call methyl-orange titration.

(b) Add 2 drops of methyl-orange if the phenolphthalein fails to turn the solution red, and then add N/50 sulphuric acid until a faint pink occurs. Record the number of cc. used, and call methyl-orange titration.

Procedure with Erythrosine.

In place of methyl-orange, erythrosine may be used. Using it the procedure is as follows:—

To 50 cc. (or 100 cc. if alkalinity is low) of the water in a 250 cc. glass stoppered bottle, add 4 drops of phenolphthalein indicator. If it turns red proceed as in (a) above down to where methyl-orange is added. Then proceed as follows:—Add 5 cc. of neutral chloroform and 1 cc. of erythrosine (0.5 grm. of sodium salt in 1 litre of distilled water). On shaking the solution becomes rose coloured. Add acid until the solution becomes colourless. Record the number of cc. used. This can be designated the "methyl-orange titration" in conformity with the above, the erythrosine giving all that the methyl-orange would.

If there is no phenolphthalein alkalinity proceed at once with erythrosine as indicated.

Bicarbonates.

The alkalinity is due to bicarbonates alone when phenolphthalein gives no colouration when added to the water. The number of cc. of acid used with methyl-orange $\times 20$ (or 10 if 100 cc. of water are used) give parts per million CaCO_3 as bicarbonate alkalinity.

If the phenolphthalein titration is less than the methyl-orange titration, carbonates and bicarbonates are present. The phenolphthalein titration gives half the carbonates according to the following equation:— $2\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 = 2\text{NaHCO}_3 + \text{Na}_2\text{SO}_4$, while the methyl-orange titration gives all the bicarbonates already present in the water plus the bicarbonates formed from the carbonates during titration with phenolphthalein. The methyl-orange titration minus the phenolphthalein titration multiplied by 20 (or 10 if 100 cc. of water are used) gives parts per million bicarbonates in terms of calcium carbonate. The bicarbonate, carbon dioxide as bicarbonate, and half bound carbon dioxide are determined by the following factors:—

Bicarbonate (HCO_3) 1.22 times the bicarbonate expressed in terms of calcium carbonate.

Carbonic acid (CO_2) as bicarbonate 0.88 times the bicarbonate expressed in terms of calcium carbonate.

Half bound carbonic acid (CO_2) 0.44 times the bicarbonate expressed in terms of calcium carbonate.

Carbonates.

The alkalinity is due solely to normal carbonates when the phenolphthalein titration is equal to the methyl-orange titration. The number of cc. of N/50 sulphuric acid used with phenolphthalein multiplied by 40 (or by 20 when 100 cc. of water are used) gives the parts per million of carbonates in terms of calcium carbonate. When the phenolphthalein titration is less than the methyl-orange titration, bicarbonates and carbonates are present. The carbonate alkalinity expressed in parts per million of calcium carbonate is equal to the phenolphthalein titration multiplied by 40. When the phenolphthalein titration is greater than the methyl-orange titration, carbonates and

hydroxides are present. During the phenolphthalein titration the hydrates and half the carbonates are neutralised, while during the methyl-orange titration the bicarbonates, formed from the carbonates are neutralised. The methyl-orange titration multiplied by 40 (or 20 when 100 cc. of water are used) gives the carbonates in parts per million in terms of calcium carbonate. The carbonate, carbonic acid as carbonate, and bound carbonic acid are determined from it by the following factors:—

Carbonate (CO_3) 0.6 times the normal carbonates expressed in terms of calcium carbonate.

Carbonic acid as carbonate (CO_2) 0.44 times the normal carbonates expressed in terms of calcium carbonate.

Bound carbonic acid (CO_2) is the sum of the carbonic acid as carbonate plus one-half that as bicarbonate.

Hydroxides.

When hydroxides are present the phenolphthalein titration is greater than the methyl-orange titration. If there is no methyl-orange titration, the alkalinity is due solely to hydroxides. This is indicated when the solution turns pink upon the addition of methyl-orange at the completion of the phenolphthalein titration. The number of cc. $\text{N}/50 \text{ H}_2\text{SO}_4$ used for phenolphthalein $\times 20$ (or 10 if 100 cc. of water are used) gives the hydroxides in parts per million in terms of CaCO_3 . When phenolphthalein titration is greater the number of cc. used with phenolphthalein minus the cc. used with methyl-orange times 20 (or 10 when 100 cc. of water are used) gives parts per million hydroxides in terms of CaCO_3 .

The following table expresses the above in a more compact form, and will no doubt prove useful:—

Table showing Calculation of Alkalinity from Phenolphthalein and Methyl-orange or Erythrosine Titration when using 50 cc. of Water.

	Bicarbonates.	Carbonates.	Hydroxides.
P* = O	20M	O	O
P = M	20(M-P)	40P	O
P = M	O	40P	O
P M	O	4OM	20(P-M)
M† = O	O	O	20M

* P = Phenolphthalein titration.

† M = Methyl-orange titration.

—Chemical Engineer, xxii., No. 6.

SIMPLE SODIUM LAMP FOR POLARISCOPE.

By G. K. FORESMAN.

SPECIAL lamps to produce a sodium flame for polariscopes are all expensive and more or less troublesome to adjust and maintain in working order. A simple, cheap, and satisfactory substitute is here suggested.

It consists of a piece of fire and acid proof asbestos board about four inches square and one-eighth of an inch thick, with a slit $3 \times \frac{1}{4}$ inch and one inch from the edge cut in the asbestos. This is used in connection with an ordinary Bunsen burner with wing-top. The asbestos board is supported about a quarter of an inch above the wing-top by means of a burette clamp, the burner being directly under the middle of the slit and parallel to it.

The flame burns around the edges of the slit, forming a broad double flame, which is easy to locate with the instrument and of greater intensity than the usual flame. Salt is added around the edge of the slit as a saturated solution by means of a pipette. The sides of the asbestos board may be bound with metal to support it at the ends of the slit. When one slit burns out another may be cut in the same piece of asbestos board, back of the first. The asbestos does not seem to affect the quality of the sodium flame.—*Journal of Industrial and Engineering Chemistry*, viii., No. 2.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 17, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Action of Cobra Venom." By A. R. CUSHNY, F.R.S., and S. YAGI.

Part I.—The action of cobra venom has generally been supposed to be exerted in part on the central nervous system, in part on the terminations of the motor nerves. It is shown that there are no symptoms of central nervous action in either cold or warm-blooded animals, and that death occurs from paralysis of the motor nerve terminations in striated muscle. In the frog this is accompanied by slowness, and finally arrest of the circulation from a direct action on the heart. In mammals the failure of the respiration is due to the paralysis of the respiratory nerve terminations, but this is often accompanied by the inhalation of saliva, which accelerates asphyxia. The heart is also weakened by quantities of venom greater than the minimum lethal dose. A number of antidotes were examined without any great success, because no antidote appeared capable of ejecting the venom from its combinations in the tissues.

Part II.—The action on the peripheral organs was found to consist in a preliminary phase of stimulation followed by paralysis of muscle, whether striated or unstriated. This is common to all forms of muscle whatever the nature of its innervation, so that it cannot be attributed to action on the nerve ends. The sympathetic ganglia and the secretory epithelium did not appear to be affected by the venom.

"Gametogenesis and Sex-determination in the Gall-fly, *Neuroterus lenticularis*." Part III. By LEONARD DONCASTER, F.R.S.

"Structure and Development of the Skull and Laryngeal Cartilages of *Perameles*, with Notes on the Cranial Nerves." By PHILIPPA C. ESDAILE.

"Physiological Investigations with *Petiole-Pulvinus* Preparation of *Mimosa pudica*." By J. C. BOSE and S. C. DAS.

THE following statement as to the steps taken by the Royal Society with respect to Lord Derby's Scheme of Recruiting is issued to the Fellows at the request of the Council:—

The Council of the Royal Society has been impressed by the necessity of maintaining the scientific efficiency of the nation throughout the present critical period of our history, so as to safeguard the future as far as possible. Renewed importance having been given to the question by Lord Derby's recruiting scheme, the Council now consider the time opportune for issuing to its Fellows a confidential statement in view of the steps they have taken.

It has been the desire of the Council to secure that scientific men serving in His Majesty's Forces should if possible be attached to units or employed in work in which their scientific training is of use, and for this purpose they have, as mentioned in the last Annual Report, formed, with the help of universities and scientific societies, a classified list of men serving at the front. This list is now being extended so as to include those who have attested under Lord Derby's scheme.

In certain branches of science, however, there can be no question that men can be more usefully employed at home in work connected with the war, and although it is not directly concerned in maintaining the educational efficiency of the universities, the Royal Society cannot fail to recognise that the national prosperity after the war

must depend to a great extent on the reserve of power of research and teaching that will be left in the country. The officers of the Society have, therefore, at the request of the Council, entered into communication with the "Reserved Occupations Committee," with the Committee of the Ministry of Munitions which regulates the distribution of war badges, and with the Board of Education.

In consequence of the representations made the Government have included in the list of "reserved occupations" the provision that analytical and research chemists cannot be called upon to serve in the Forces without the consent of the Royal Society. The Society has also been assured that agricultural chemists are covered by this regulation. In order to decide on such cases as may be referred to them by the local tribunals for decision, the Council have appointed a Committee on which the Chemical Society, the Society of Chemical Industry, the Institute of Chemistry, and the Society of Public Analysts are represented by their Presidents.

In order to keep the scientific laboratories supplied with men carrying on research in connection with the war, and assistants or mechanics indispensable in such work, the Royal Society has received for distribution a number of badges which they are authorised to distribute to those men who devote substantially the whole of their time to war work, are of military age, and have not been rejected on medical grounds (in which case they are entitled to an armlet). A considerable number of these badges have already been distributed.

A body of microscopists, nominated by the Royal Society, for protozoological and bacteriological work under the War Office or Admiralty, have been afforded protection by the issue of badges. The local tribunals have no power to enlist the holders of such badges without the authority of the central tribunal in London.

Although it might have been desirable to extend the provision regarding chemists referred to above to other branches of science, this was not found to be possible, but the Board of Education has undertaken to consider special cases submitted by university and other institutions of higher scientific and technical education in which it is desirable, in the interests of national efficiency as regards education and research, to retain scientific men of military age for scientific work not immediately concerned with the production of munitions of war. In this matter the Royal Society and the Board of Education are keeping in close touch with each other.

The continuous increase of scientific work connected with the war renders it necessary to keep up the supply of men capable of doing such work, and this is—at any rate partially secured by an arrangement between Lord Derby's Committee and the Board of Education, according to which third-year students at universities will not be called up. This provision is now also being extended to university teachers considered to be indispensable, and the Board of Education is prepared to consider any special cases submitted to them by the Royal Society.

A. SCHUSTER, } Secretaries, R.S.
W. B. HARDY, }

February, 1916.

PHYSICAL SOCIETY.

Annual General Meeting, February 11, 1916.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

The report of the Council was read by the SECRETARY.

The report of the Treasurer was read by Mr. DUDELL. Both reports were unanimously adopted.

Votes of thanks to the Auditors, to the Officers and Council, and to the Governing Body of the Imperial College were carried unanimously, the respective proposers and seconders being Prof. HOWE and Mr. ADDENBROOKE, Dr. HARKER and Principal SKINNER, and Dr. RUSSELL and Dr. CHREE.

The following is the list of officers elected for the ensuing year:—

President—Prof. C. Vernon Boys, F.R.S.,

Vice-Presidents (who have filled the office of President

—Prof. G. C. Foster, F.R.S.; Prof. R. B. Clifton, M.A., F.R.S.; Prof. A. W. Reinhold, C.B., M.A., F.R.S.; Sir W. de W. Abney, R.E., K.C.B., D.C.L., F.R.S.; Prin. Sir Oliver J. Lodge, D.Sc., F.R.S.; Prof. S. P. Thompson, D.Sc., F.R.S.; R. T. Glazebrook, D.Sc., F.R.S.; Prof. J. Perry, D.Sc., F.R.S.; C. Chree, Sc.D., F.R.S.; Prof. H. L. Callendar, M.A., F.R.S.; Prof. A. Schuster, Ph.D., F.R.S.; Sir J. J. Thomson, O.M., D.Sc., F.R.S.

Vice-Presidents—W. R. Cooper, M.A., B.Sc.; F. E. Smith; S. W. J. Smith, M.A., D.Sc., F.R.S.; W. E. Sumpner, D.Sc.

Secretaries—W. Eccles, D.Sc.; R. S. Willows, M.A., D.Sc.

Foreign Secretary—R. T. Glazebrook, D.Sc., F.R.S.

Treasurer—W. Duddell, F.R.S.

Librarian—S. W. J. Smith, M.A., D.Sc., F.R.S.

Other Members of Council—H. S. Allen, M.A., D.Sc.; Prof. W. H. Bragg, M.A., F.R.S.; S. G. Chalmers, M.A.; Prof. G. W. O. Howe, D.Sc.; Prof. J. W. Nicholson, M.A., D.Sc.; C. C. Paterson; C. E. S. Philipps, F.R.S.E.; Prof. O. W. Richardson, M.A., D.Sc., F.R.S.; G. F. C. Searle, Sc.D., F.R.S.; F. J. W. Whipple, M.A.

At the conclusion of the general business the chair was taken by the President, Prof. C. V. Boys, F.R.S., and the following papers were read:—

"On a General Bridge Method for Comparing the Mutual Inductance between Two Coils with the Self-inductance of One of Them," by Prof. C. H. LEES, F.R.S.

It is shown that the self-inductance L of a coil of resistance S may be compared with the mutual inductance M between the coil, and another by making the first coil one arm of a bridge, PQRS, of which the second coil and a resistance $U+V$ in series form one diagonal, the galvanometer forming the other. The cell is connected through a key to the point of contact of U and V . When the steady balance has been obtained U or V can be varied so as to get an induction balance for any value of L/M without P, Q, R , or S having to be changed. Then $L/M = -(Q+S)/(1+Q/PV)/(T+U)$.

DISCUSSION.

Dr. A. RUSSELL said that the author's arrangement was a great improvement on Maxwell's original method. As a student at the Cavendish Laboratory, he had experienced great difficulty with that method. The greatly increased accuracy in inductance measurements due to the use of vibration galvanometers had led to neglect of the older methods, but some of them would be useful in special cases. He asked the author why in his final formula he had made the mutual inductance negative.

Principal SKINNER said that he had also found difficulty with Maxwell's method, and congratulated Prof. Lees on the simplicity of the apparatus required in his modification.

Mr. W. DUDELL welcomed an addition to the methods of measuring inductance. The more alternative methods available for checking results the better.

Prof. HOWE suggested that T and N should be inserted in the figures as well as in the text. He thought Figs. 2 and 3 should be drawn in a similar way to show their close correspondence.

The PRESIDENT said that he had always experienced trouble in obtaining a balance with Maxwell's arrangement, and he was relieved to find that similar difficulty had been experienced by workers in the Cavendish Laboratory.

The AUTHOR, in reply, said he had simply followed Maxwell with regard to the negative sign of the mutual inductance. He would be pleased to make the alterations to Fig. 3 suggested by Prof. Howe.

"An Enclosed Cadmium-vapour Arc Lamp," by Dr. H. J. S. SAND.

The lamp shown was similar in general principle to the

well-known mercury lamp. It is constructed of quartz glass. To start the lamp the metal is melted by means of a Bunsen burner, and the arc struck by tilting. Before introduction into the lamp the metal is freed from oxide and dissolved gases by a special process of filtration while at the pump. It is prevented from adhering to the glass, which might lead to fracture, by the presence of a small amount of a loose powder in the lamp. The lamp gives a powerful light, and once started will continue burning indefinitely.

DISCUSSION.

Dr. J. A. HARKER mentioned that when Benoit and Michelson were performing their celebrated experiments on the length of the metre in terms of the wave-length of light it was necessary to make up a large number of cadmium vacuum tubes. One of these only lasted about one day. The light was incomparably poorer than that given by the author's lamp, and the windows were constantly becoming obscured with condensed metal.

Dr. R. S. WILLOWS said he had seen this lamp working satisfactorily for four or five hours on end. For diffraction experiments it was of the greatest importance to have really strong sources of monochromatic light. With suitable filters the cadmium lamp would prove extremely useful for such purposes.

Dr. T. M. LOWRY, in a written communication which was read by the Secretary, expressed a high opinion of the utility of the cadmium arc lamp. He had used one of Dr. Sand's lamps for over a year, and for laboratory purposes there was no particular in which it could be improved. Five years of additional experience had confirmed the conclusion which he had come to in 1909, that the best series of lines for exploring all the chief regions of the visible spectrum is obtained by combining the arc spectrum of mercury and cadmium with the flame spectra of lithium and sodium. The complete series of lines was as follows:—

Li, 6708; Cd, 6438; Na, 5893; Hg, ⁵⁷⁶⁹₅₇₉₀; Hg, 5461;
Cd, 5086; Cd, 4800; Cd, 4678; Hg, 4358.

His own experiments on the production of a strong cadmium spectrum had been described elsewhere, and if, as he believed, these had helped to stimulate Dr. Sand in his endeavour to produce a practical arc, their publication had been even more fully justified than he had hoped.

The PRESIDENT asked if the cadmium vapour arc acted as a rectifier in the same way as the mercury arc.

Two slides were shown by Dr. S. RUSS. The first of these showed the ultra-violet spectrum of the Simpson arc, compared with that of carbon. This arc is a very strong source of ultra-violet light, giving a practically continuous spectrum with all but very short exposures. With a short exposure the lines are seen to be very close together, and to be beautifully graded in intensity. The electrodes are said to be made from wolframite, the chief constituent of which is tungsten. The next slide showed the ultra-violet spectrum of pure tungsten compared with the Simpson arc. From this it was evident that the spectrum of the latter was almost wholly due to tungsten.

The Royal Society.—The following are the names of the fifteen selected candidates for election into the Royal Society on May 11 next:—E. H. Barton, W. R. Bousfield, S. G. Brown, E. G. Coker, A. G. Henderson, J. E. Littlewood, A. McKenzie, J. A. MacWilliam, J. H. Maiden, H. H. W. Pearson, J. A. Pollock, L. Rogers, C. Shearer, D'A. W. Thompson, and H. Woods.

Literary Intelligence.—Messrs. J. and A. Churchill are just publishing a translation, by Dr. Martin H. Fischer, Professor of Physiology, University of Cincinnati, of Dr. Wolfgang Ostwald's "Handbook of Colloid Chemistry: the Recognition of Colloids, Theory of Colloids, and their general Physico-Chemical Properties."

NOTICES OF BOOKS.

Physical Chemistry for Schools. By HENRY JOHN HORSTMAN FENTON, M.A., Sc.D., F.R.S. Pp. viii.+215. Price 3s. 6d. net. Cambridge: The University Press. 1916.

THIS book has been written as an introduction to physical chemistry for students who have been through elementary courses of descriptive chemistry and physics. The leading principles of the theory of solutions, electrochemistry, thermochemistry, &c., are well explained, and clear and precise ideas could be obtained from the book, while the subject is presented in a very interesting manner and moreover is made as easy as possible. The essential features of the theory of solutions, for example, and the nature and properties of alloys are admirably put before the student, and many difficulties are forestalled. It seems probable that it would be better to regard the book as accompanying a descriptive course rather than following it; most of the chapters on atomic weights and the Periodic Table, for instance, could be taken quite early, as well as that on elements, mixtures, and compounds. On the other hand some parts require a fair knowledge of the properties and behaviour of many substances, and a somewhat different arrangement of the chapters might have been advisable. However, the teacher could probably make his own alterations in that respect without much difficulty, and the book is undoubtedly on the right lines for promoting thoroughness and accuracy in elementary scientific education.

Questions and Numerical Exercises in Physics and Chemistry. By DAVID BAIRD, M.A. Pp. 103. Price 1s. net. London, Glasgow, and Bombay: Blackie and Son, Ltd. 1915.

THE questions in this book cover the ground of the Intermediate Leaving Certificate in Science of the Scotch Education Department. Some typical numerical examples are worked out in full, and in a few cases notes and definitions are provided. The course in physics includes measurements of physical constants and elementary heat, while in chemistry easy questions are given on physical and chemical changes—air, water, chalk, &c. The order of the sections and of the questions in each section follows that in which the subjects are usually studied, and in every respect the work of a skilled and experienced teacher is evident. Although the questions conform more or less to the usual type and exhibit no particular novelty they will provide a good test both of the student's knowledge and of his power of applying it, equally useful for revision or for working through as the course of study proceeds. The book contains a few tables of physical constants, and answers to the numerical examples are given.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 2, January 10, 1916.

This number contains no chemical matter.

No. 3, January 17, 1916.

Fluorine in the Vegetable Kingdom.—Armand Gautier and Paul Clausmann.—The authors have determined the amounts of fluorine and phosphorus in various parts of plants, paying special attention to those plants or parts of plants which are used as food for men or animals. The leaves are the richest in fluorine, the stem, root, and

bark containing the least. Soft fruits (eatable portion) are fairly rich in fluorine, and the pulp when dried always contains less than the skin. There appears to be no simple law connecting the amounts of fluorine and phosphorus in the different organs of a plant, but the two elements usually increase and diminish together.

Formation of Pyridine and Isoquinoline Bases starting from Casein.—Amé Pictet and Tsan Quo Chou.—Casein was heated for about six hours with hydrochloric acid on the water-bath, and methylal was allowed to drop in drop by drop during the operation. Methylal is decomposed by mineral acids into formic aldehyde and methyl alcohol, and thus the casein was hydrolysed in presence of a permanent source of formic aldehyde. The acid solutions were evaporated to dryness and distilled with quicklime. The product was a yellowish oil which dissolved practically entirely in dilute hydrochloric acid. The solution, which contained primary, secondary, and tertiary bases, was freed from the two former by means of sodium nitrite. The tertiary bases were subjected to fractional distillation, and the following were thus isolated:—Pyridine, 2,6-dimethyl-pyridine, another base of formula C_7H_9N , of undetermined composition; isoquinoline, 4-methylisoquinoline; a base, $C_{11}H_{11}N$ (probably an ethyl or dimethylisoquinoline), and a base $C_{12}H_{13}N$. No trace of quinoline was detected. These bases were not obtained if methylal was not added.

Nitration of Phenylpropionic Acid.—S. Reich.—When phenylpropionic acid is added gradually to nitric acid, cooled to -20° , paranitro-phenylpropionic acid is obtained. If the nitration is carried out at 0° this acid is accompanied by a small quantity of its ortho isomer. No meta acid is formed in these conditions.

Displacement of Potash and Phosphoric Acid contained in certain Rocks by Substances employed as Manures.—G. André.—Various salts employed as manures or normally present in the soil are capable of liberating potash and phosphoric acid from rocks containing them by prolonged trituration in presence of distilled water. Chalk, common salt, and calcium sulphate produce about the same effect, while sodium nitrate and ammonium sulphate liberate larger quantities of potash. Very similar results are obtained with apatite.

No. 4, January 24, 1916.

Comparative Action of Saccharose and Invert Sugar on Cupropotassic Liquid. L. Maquenne.—The author has already pointed out that saccharose is much more sensitive than invert sugar to variations of temperature and the duration of heating with cupropotassic liquid. He has now studied the question in greater detail, and gives curves showing the comparative results of the influence of temperature and duration of heating.

Bulletin de la Société Chimique de France.
Vol. xvii.-xviii., No. 23-24, 1915.

Characterisation of Chlorinated Ketones.—E. E. Blaise.—Generally speaking it is difficult to transform chlorinated ketones into solid derivatives for the purpose of identifying them, but the author has found that their normal semicarbazones possess melting-points which are low enough to be conveniently determined for identification. If a solution of a molecule or a molecule and a half of semicarbazide hydrochloride in water is added to a chlorinated ketone, the latter is rapidly converted into semicarbazone, the only exception being trichloromethylmethyl ketone. In order to purify the semicarbazone it must be washed in water, benzene, and chloroform successively. It is then heated on the water-bath with a large quantity of benzene or chloroform, the temperature not being allowed to exceed 50° . A small quantity of sodium sulphate is added, the solution is filtered, and the semicarbazone is allowed to crystallise.

Removal by Water of the Nitrogenous and Mineral Matter contained in Leaves.—G. André.—The nutritive materials contained in leaves must be gradually returned to the soil when they fall in autumn. When living the leaf is very impervious to water, but this is not the case when it is detached from its stalk and completely immersed in water. Gradually exosmosis of the phosphates, potassium, calcium, and magnesium salts which it contains occurs, and some of the nitrogen is converted into the soluble form. The author has found that the fertilising materials in the leaves are returned to the soil with very unequal velocities. Considering only the leaves of the chestnut the author finds that about 1/15 to 1/20 of the nitrogen and 70 to 75 per cent of the phosphoric acid is converted into the soluble form. As for the potassium almost all of it is set free. From a lengthy series of experiments he found that after six months the exosmosis of the nitrogen had reached 6.32 per cent of the total nitrogen in the youngest leaves and 2 per cent in the oldest leaves. The exosmosis of the phosphorus (calculated as PO_4H_3) is 50 per cent after six months, while in young leaves the potassium is almost entirely eliminated and made up to 87 per cent in older leaves.

Vol. xix.-xx., No. 1, 1916.

Analysis of a Mixture of Alkaline Sulphides, Hyposulphites, and Dithionates.—J. A. Muller.—To determine sulphur present as sulphides and hyposulphites the author first titrates with iodine, using a very dilute solution slightly acidified with acetic acid. He then keeps some of the solution in a vacuum for about ten minutes, meanwhile thoroughly shaking. The dissolved sulphuretted hydrogen is thus totally expelled, and the liquid is then again titrated with iodine. The thionates present do not interfere in these titrations. To determine the sulphur present as thionate an aliquot part of the liquid if acidified with acetic acid, the sulphuretted hydrogen is expelled *in vacuo* as before, the sulphide of antimony is separated off, the liquid is made alkaline with potash, and the mixture is then evaporated to dryness with a little nitre. All the sulphur present is thus converted into the state of sulphate, and may be determined as barium sulphate. By subtracting the amount corresponding to the sulphates and hyposulphites present the thionates are determined.

Syntheses by means of Mixed Organometallic Derivatives of Zinc. Preparation of α -Ketonic Acids.—E. E. Blaise.—To prepare α -ketonic acids oxisobutyric acid is treated with ethoxalyl chloride, and the raw product is heated with thionyl chloride. The condensation of the acid chloride thus obtained with a mixed organic metallic derivative of zinc gives the mixed cycloacetal the desired α -ketonic acid. The cycloacetal itself is very easily decomposed by alcoholysis on the water-bath. Thus a mixture of oxisobutyric ether and α -ketonic ether is obtained, and the constituents can readily be separated by fractional distillation. A small quantity of the acet corresponding to the ketonic ether is formed at the same time.

MEETINGS FOR THE WEEK.

- MONDAY, 6th.—Royal Institution, 5. (General Meeting).
TUESDAY, 7th.—Royal Institution, 3. "The Plant and the Soil Man's Control," by Dr. E. J. Russell.
— Röntgen Society, 8.15. Discussion on "The Injurious Effects produced by X rays." "The Use of Inverse Current," by A. C. Gunstone.
THURSDAY, 9th.—Royal Institution, 3. "Recent Excavations in Mesopotamia—The Southern Capital, Babylon," Prof. L. W. King.
— Royal Society. "Distribution of Intensity Broadened Spectrum Lines," by J. W. Nicholson and T. R. Merton. "On Professor Joly's Method of Avoiding Collision at Sea," by H. C. Plummer.
FRIDAY, 10th.—Royal Institution, 5.30. "Illusions of the Upper Air," by Sir Napier Shaw.
SATURDAY, 11th.—Royal Institution, 3. "Radiations from Atoms Electrons," by Sir J. J. Thomson.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2937.

A SIMPLE METHOD FOR VAPOUR-DENSITY DETERMINATIONS.

(PART XIII.).

By PHILIP BLACKMAN.

(Continued from p. 76).

If the manometer be bent round the apparatus becomes more compact (Fig. 5), and enables one to use a longer bulb. This form should be found especially useful when suspension is desirable.

Note to all Parts.—When *l* has been determined the bulb is opened by cutting away a small portion at the clear end and water is poured in from a burette to determine

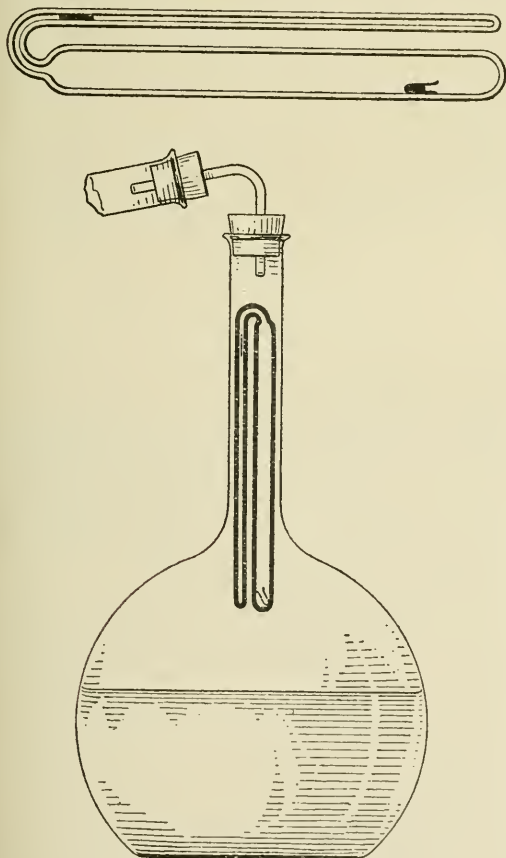


FIG. 5.

its volume (*V*). The same apparatus may be used for any number of determinations if after each experiment the closed end of the capillary tube is cut off and the whole thoroughly cleaned and dried. For all general purposes the original apparatus (*i.e.*, with a detached manometer inside) is much the simpler in manipulation, because of its convenient size and the absence of fusing on the manometer.

RESULTS.

<i>w.</i> Grm.	<i>l.</i> Mm.	<i>t</i> ₁ °C.	<i>p.</i> Mm.	<i>V.</i> Cc.	<i>L.</i> Mm.	<i>L</i> _c Mm.	Vapour-density.	
							Found.	Theory.
CCl ₄ .								
0.1791	360	17.5	753	150.3	425	430	74.31	76.90
0.1933	349	17.5	756	148.2	418	423	74.32	76.90
0.1612	354	17.5	756	145.3	412	418	74.35	76.90
0.1885	344	18.0	756	144.0	409	418	74.37	76.90
0.1759	340	18.0	761	140.0	400	410	74.30	76.90
0.2088	321	18.0	760	137.9	394	400	74.30	76.90
0.1651	333	18.0	758	134.8	391	400	74.30	76.90
0.1881	319	18.5	758	130.8	388	394	74.30	76.90
0.1972	310	17.5	754	126.0	381	390	74.32	76.90
0.2243	300	17.0	757	123.8	377	390	74.37	76.90
0.1583	312	16.5	761	120.7	372	380	74.35	76.90
0.1449	310	16.5	763	116.8	366	372	74.34	76.90
0.1269	312	16.0	766	112.3	360	369	74.30	76.90
0.1123	315	16.5	767	109.4	360	367	74.30	76.90
0.1159	300	16.5	763	105.3	354	358	74.36	76.90
0.1228	300	17.0	758	100.9	310	360	74.37	76.90
0.1297	290	16.5	754	96.0	348	357	74.31	76.90
0.1083	295	16.0	756	93.3	343	351	74.33	76.90
0.1271	283	16.5	758	90.1	340	350	74.30	76.90
0.1271	275	17.5	760	87.3	334	349	74.30	76.90
C ₆ H ₆ .								
0.5672	163	17.5	750	180.1	320	323	38.97	39.00
0.5887	160	17.0	755	178.8	318	325	38.94	39.00
0.6604	148	18.0	755	176.8	316	320	38.97	39.00
0.5864	153	18.0	754	170.8	310	320	38.93	39.00
0.6044	149	18.5	755	165.8	313	320	38.95	39.00
0.6111	147	19.0	759	160.7	310	329	38.96	39.00
0.6096	140	19.0	758	159.3	300	310	38.97	39.00
0.6562	136	19.5	760	156.0	306	319	38.97	39.00
0.6080	141	20.0	761	154.2	309	315	38.97	39.00
0.5151	150	19.5	763	151.5	310	318	38.94	39.00
0.5589	143	20.0	763	148.9	305	310	38.97	39.00
0.6279	131	19.5	764	145.7	300	308	38.95	39.00
0.5464	138	18.0	764	142.4	297	301	38.96	39.00
0.5656	132	18.0	764	140.1	290	297	38.96	39.00
0.3941	180	16.5	761	186.6	293	299	38.93	39.00
0.3392	189	16.0	759	184.6	288	295	38.97	39.00
0.3430	184	16.5	758	180.1	287	293	38.95	39.00
0.3878	172	17.0	757	170.3	284	290	38.97	39.00
0.3650	173	17.5	758	170.4	280	291	38.97	39.00
0.3700	171	17.5	758	165.3	281	293	38.97	39.00
CHCl ₃ .								
0.3568	205	17.5	760	190.4	280	285	58.99	59.67
0.3668	201	18.5	760	189.0	277	281	58.94	59.67
0.3623	200	18.0	757	186.3	276	280	58.90	59.67
0.3598	196	18.5	758	184.2	270	275	58.97	59.67
0.3722	194	18.5	755	180.9	271	277	58.96	59.67
0.3181	199	19.0	753	176.5	268	274	58.90	59.67
0.2993	201	20.0	758	170.3	270	274	58.98	59.67
0.3278	194	19.5	761	165.8	265	274	58.97	59.67
0.3802	180	19.5	763	160.3	261	269	58.91	59.67
0.3004	189	19.0	761	158.2	258	263	58.94	59.67
0.2369	199	17.5	760	156.8	255	261	58.95	59.67
0.3510	176	18.0	759	154.5	250	260	58.97	59.67
0.3406	181	17.5	754	150.0	257	268	58.96	59.67
0.3524	174	18.0	757	147.8	254	260	58.98	59.67
0.2996	180	18.0	757	143.9	251	258	58.99	59.67
0.3991	163	18.5	760	142.1	248	259	58.94	59.67
0.3276	159	19.0	758	141.1	244	251	58.91	59.67
0.2785	174	19.5	759	137.4	240	248	58.97	59.67
0.2879	170	18.5	761	134.4	238	246	58.94	59.67
0.2792	165	19.0	761	132.1	230	238	58.93	59.67
C ₅ H ₅ N.								
0.5461	120	20.0	758	185.3	230	235	37.73	39.50
0.5556	115	19.5	761	180.2	224	230	37.80	39.50
0.5830	110	19.5	761	178.1	221	227	37.75	39.50
0.4987	116	18.0	763	175.3	217	222	37.74	39.50
0.4966	111	20.0	765	170.0	210	216	37.80	39.50

C_3H_5N (continued).

w.	l.	t ₁ .	p.	V.	L.	L _c .	Vapour-density.	
							Found.	Theory.
Grm.	Min.	°C.	Mm.	Cc.	Mm.	Mm.		
0.4950	109	17.0	760	165.0	208	215	37.80	39.50
0.4977	105	16.0	759	161.3	203	210	37.75	39.50
0.6291	100	17.0	755	188.5	200	210	37.75	39.50
0.6991	91	17.5	754	183.6	196	207	37.75	39.50
0.7664	87	17.0	759	180.7	200	208	37.75	39.50
0.6185	93	18.5	760	177.7	191	200	37.75	39.50
0.5994	93	18.0	760	173.7	187	199	37.75	39.50
0.6075	88	18.5	760	170.6	184	190	37.79	39.50
0.2412	224	18.5	764	165.8	320	329	37.80	39.50
0.2849	212	17.0	760	161.9	317	325	37.74	39.50
0.3044	202	17.0	758	188.1	310	321	37.73	39.50
0.3342	188	16.5	757	185.3	310	322	37.75	39.50
0.3137	194	17.0	760	180.0	308	316	37.75	39.50
0.3222	186	18.0	754	175.7	302	310	37.75	39.50
0.3106	176	20.0	759	172.8	300	311	37.78	39.50

 $C_3H_{11}OH$.

w.	l.	t ₁ .	p.	V.	L.	L _c .	Found.	Theory.
Grm.	Min.	°C.	Mm.	Cc.	Mm.	Mm.		
0.4410	210	15.5	758	170.3	359	365	42.18	44.00
0.4030	215	16.0	759	165.8	356	365	42.25	44.00
0.3691	220	16.0	763	160.1	356	365	42.20	44.00
0.3852	212	16.5	764	158.3	350	360	42.20	44.00
0.3454	218	17.5	760	152.5	352	360	42.22	44.00
0.3065	225	17.0	758	150.7	347	358	42.19	44.00
0.3142	240	17.5	758	182.3	350	360	42.21	44.00
0.3816	220	18.5	757	180.9	343	357	42.18	44.00
0.2823	239	20.0	758	175.6	344	350	42.23	44.00
0.3200	225	19.5	761	172.2	340	345	42.22	44.00
0.3476	215	19.0	758	169.9	336	342	42.19	44.00
0.3497	210	19.5	757	165.4	330	340	42.24	44.00
0.3334	213	19.0	755	161.4	335	340	42.25	44.00
0.2707	220	18.5	756	153.3	325	333	42.19	44.00
0.2623	222	17.5	756	151.1	327	333	42.20	44.00
0.2721	230	17.0	760	179.6	323	330	42.20	44.00
0.2325	235	16.0	761	173.4	318	325	42.22	44.00
0.2229	231	20.0	761	169.2	310	320	42.21	44.00
0.2451	227	18.5	760	165.2	315	325	42.24	44.00
0.2526	221	16.5	760	162.1	310	321	42.20	44.00

 $(CH_3CO)_2O$.

w.	l.	t ₁ .	p.	V.	L.	L _c .	Found.	Theory.
Grm.	Min.	°C.	Mm.	Cc.	Mm.	Mm.		
0.3105	250	17.0	761	188.3	341	350	50.09	51.00
0.2780	256	17.0	760	184.5	340	350	50.08	51.00
0.2527	261	18.0	758	181.3	339	350	50.10	51.00
0.2377	255	17.5	763	178.2	330	337	50.11	51.00
0.2003	263	19.0	766	175.9	326	336	50.07	51.00
0.1888	260	19.0	769	171.9	328	339	50.11	51.00
0.1537	271	20.0	749	165.9	327	333	50.12	51.00
0.1150	275	20.0	751	163.2	316	323	50.09	51.00
0.2728	241	19.5	758	191.4	318	325	50.10	51.00
0.2740	245	19.0	767	190.6	320	331	50.09	51.00
0.2082	252	17.5	760	186.0	310	321	50.12	51.00
0.1924	249	16.0	764	181.0	306	312	50.11	51.00
0.2318	255	17.5	765	181.2	308	318	50.10	51.00
0.1362	261	16.5	763	176.3	300	310	50.10	51.00
0.1338	263	17.0	759	174.5	300	311	50.07	51.00
0.0897	271	16.5	756	171.8	294	306	50.08	51.00
0.1112	266	16.5	759	166.2	295	310	50.11	51.00
0.0932	265	17.5	758	164.3	291	302	50.10	51.00
0.0839	262	18.0	761	162.3	287	295	50.10	51.00
0.0753	264	19.5	765	160.3	288	294	50.11	51.00

 C_3H_5OH .

w.	l.	t ₁ .	p.	V.	L.	L _c .	Found.	Theory.
Grm.	Min.	°C.	Mm.	Cc.	Mm.	Mm.		
0.2405	210	16.5	758	190.4	310	319	28.74	29.00
0.1967	215	18.0	760	187.3	305	310	28.74	29.00
0.2046	210	18.5	761	184.5	307	309	28.74	29.00
0.1808	219	19.0	764	180.8	306	311	28.73	29.00
0.1655	221	19.0	767	176.3	296	305	28.75	29.00
0.1569	213	19.0	766	174.2	294	305	28.75	29.00
0.1929	206	20.0	766	171.1	296	305	28.73	29.00
0.1862	212	19.5	765	191.7	290	300	28.76	29.00
0.1799	215	18.5	760	190.0	293	302	28.74	29.00
0.1888	208	17.0	758	187.5	289	297	28.74	29.00

 C_3H_5OH (continued).

w.	l.	t ₁ .	p.	V.	L.	L _c .	Found.	Theory.
Grm.	Min.	°C.	Mm.	Cc.	Mm.	Mm.		
0.1603	208	16.5	757	184.2	277	285	28.75	29.00
0.1624	203	16.0	754	180.3	273	281	28.74	29.00
0.1896	195	16.0	754	176.3	275	285	28.76	29.00
0.1712	199	16.5	749	174.1	271	285	28.73	29.00
0.1454	201	17.5	750	170.8	269	274	28.74	29.00
0.2167	180	19.0	751	189.2	260	270	28.74	29.00
0.2085	182	18.5	753	185.3	261	271	28.73	29.00
1.1792	187	17.0	755	181.5	258	266	28.75	29.00
0.2411	171	17.5	760	179.6	262	268	28.75	29.00
0.2117	177	19.0	758	175.4	260	269	28.74	29.00

 CH_3COCl .

w.	l.	t ₁ .	p.	V.	L.	L _c .	Found.	Theory.
Grm.	Min.	°C.	Mm.	Cc.	Mm.	Mm.		
0.4680	200	19.5	758	189.6	351	360	37.94	39.22
0.4721	198	20.0	755	187.1	353	360	37.92	39.22
0.4705	199	16.0	761	184.8	351	361	37.95	39.22
0.4431	201	16.5	759	181.6	348	360	37.90	39.22
0.4559	195	19.0	758	178.0	347	357	37.96	39.22
0.4267	197	18.5	763	176.0	340	351	37.92	39.22
0.4227	191	17.5	766	173.5	330	340	37.91	39.22
0.4340	189	19.0	764	171.2	332	345	37.90	39.22
0.4058	193	20.0	757	169.1	333	345	37.95	39.22
0.3740	185	19.0	760	165.8	310	321	37.97	39.22
0.3805	184	15.5	758	163.9	312	321	37.93	39.22
0.4258	188	16.5	755	185.5	315	330	37.93	39.22
0.4334	181	17.5	761	181.5	311	320	37.94	39.22
0.3863	183	17.0	762	178.7	301	310	37.93	39.22
0.4161	178	16.5	763	175.8	305	312	37.91	39.22
0.4068	177	19.0	760	171.5	304	313	37.94	39.22
0.4237	174	19.0	760	168.3	307	316	37.90	39.22
0.3686	180	19.5	758	165.4	301	311	37.93	39.22
0.2573	174	17.5	757	161.4	305	318	37.95	39.22
0.4031	171	20.0	765	159.5	300	312	37.93	38.22

(To be continued).

THORIUM.

By THURSTON OWENS.

THREE hundred million gas mantles consumed annually throughout the world are dependent upon the supply of thorium. Some eighty million are used yearly in the United States, double the quantity consumed ten years ago. These and other valuable facts are brought out in a recent publication of the Bureau of Mines, prepared by Mr. Karl L. Kithil ("Monazite, Thorium, and Mesothorium," Technical Paper 110, Bureau of Mines, Department of the Interior, Washington).

The property of emitting light radiations in the visible part of the spectrum under the application of heat has been known and applied for over a century ("The Rare Earths: their Occurrence, Chemistry, and Technology," by S. I. Levy), but it was Dr. Auer von Welsbach who discovered (1886) that thorium had the unusual quality of holding together without other materials being used as a support; hence the mantle mesh ("Incandescent Gas Mantles." M. C. Whitaker, Johns Hopkins Lectures on Illuminating Engineering).

It was not until 1891 that Dr. Auer perfected his formula of 99 per cent thorium and 1 per cent cerium, which produced the highest light efficiency and also the nearest approach to white light in colour. For twenty-five years the mantles used by the gas industry have been produced with this formula as a base: another of the many features of continuity and stability which characterises the industry.

Thorium is one of the constituents of monazite sand, the others having great chemical interest but little commercial value (Whitaker). There are numerous occurrences of monazite sand throughout the world, but it has only been mined successfully in North and South America

(Kithil). This last statement is open to question, as the deposits at Travancore (India) have been the subject of considerable British wrath in the past few months.

"Germany, by underhand as well as straightforward methods, was steadily proceeding towards the fulfilment of her ambition to control the thorium supply of the world when war broke out." The article from which this is quoted goes on to explain how the Auer Company obtained a controlling interest in the leases at Travancore, which was nullified by an edict of the Secretary of State for India reducing the voting power of the "enemy shares" and instructing the company to sell all purchasers upon an equal basis. The British India sand which has reached this country is reported to be far superior to the Brazilian product. The mining of monazite sand in America has been practically abandoned since 1906, and none of the large users see any commercial possibilities in this field.

In order to obtain thorium two definite steps are necessary. The first consists of separating monazite from the other materials mined, which is done in the neighbourhood of the mine. The monazite sand is then shipped to the laboratories of the mantle manufacturers, where the thorium is manufactured.

"The manufacture of nitrate of thorium from monazite sand is a very difficult and complicated chemical process. It requires from four to six months to recover the small percentage of thorium and render it sufficiently pure to be used in the manufacture of lighting fluid" (Whitaker).

The treatment of monazite for the extraction of thorium described by Soddy ("The Chemistry of the Radio-Elements") is as follows:—After the sand has been ground the cold mass is dissolved in water and left to settle. The solution is then fractionally precipitated with magnesia, the thorium being concentrated mainly in the first fractions precipitated. The commonest and most useful reagent for precipitating the rare earths from a solution containing common earths, such as alumina, iron, &c., is oxalic acid. Now, thorium oxalate is of all the rare-earth oxalates the least soluble in acids, so that by working in fairly strong nitric acid solution thorium oxalate may often be precipitated and separated, at least partially, from the other rare earths and from calcium. The same is true of the rare-earth phosphates, that of thorium being one of the most insoluble in dilute acids. On the same principle thorium is often precipitated by weak bases, such as the substituted ammonias, for example dimethylamine, while zirconium, &c., remain dissolved. The potassium salt of hydrazoic acid, KN_3 , precipitates thorium hydroxide only from mixtures of thorium and cerium on boiling. The same separation may be effected by means of sodium thiosulphate on boiling, thorium alone being separated, as hydroxide. This ready hydrolysis of weak thorium is characteristic of the element. The oxalates of thorium and zirconium alone of the rare earths are soluble in ammonium oxalate, and on strongly acidifying the solution the former alone is reprecipitated. The solution of the oxalate of thorium and its conversion into soluble salts may be effected by means of concentrated ammonium or sodium carbonate and precipitation of the concentrated solution as thorium hydroxide with strong ammonium or sodium hydrate. Thorium is distinguished from the yttrium group of the rare earths by its power of forming a double sulphate with potassium sulphate, insoluble in excess of the latter reagent, and so may be separated from a mixture of the sulphates by saturating the solution with potassium sulphate. Alike in the old, now obsolete, as in the present technical methods of purifying thorium, the peculiar solubility relations of thorium sulphate in water have been largely applied. The older method consisted in volatilising the excess of sulphuric acid from the material being treated, and in dissolving the anhydrous sulphates in ice-cold water—a tedious operation—and in heating the solution till the hydrated thorium sulphate was precipitated. The latter was then dehydrated at 300° to 400° and the process re-

peated. In present practice the sulphuric acid is always kept in great excess in the initial treatment of the mineral, but the sulphate method may be employed at the final stage of manufacture as follows:—

The thorium hydroxide is dissolved in hydrochloric acid, so that the solution contains not more than 30 per cent ThO_2 , and sulphuric acid is added to the extent of 0.5 per cent more than the equivalent quantity, the temperature being kept low, and in any case below 40° as a maximum. Under these conditions the hydrate $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ is precipitated, departure from the conditions causing the separation of the tetrahydrate, which is in every way less easily manipulated. The precipitated sulphate is converted into hydroxide, and the process repeated as often as necessary to remove all impurities.

Thorium forms a curious compound with acetyl acetone, $\text{Th}(\text{C}_5\text{H}_7\text{O}_2)_4$, which is soluble in chloroform and alcohol, and can be distilled in a vacuum, and so can advantageously be employed for the purification and separation of the element.

It may be mentioned that in the fusion of refractory minerals, as with sodium carbonate, the thorium if present is converted into the highly insoluble oxide, ThO_2 , and its presence is apt to be overlooked.

Thanks largely to the thorium industry, in which a product unusually pure is essential, there exist therefor a great variety of exceedingly good and sharp methods for the separation and purification of thorium, and it must be understood that ionium if present and radio-thorium always remain unseparated from thorium in these processes as far as they have been examined.

In the manufacture of thorium nitrate from monazite a large amount of residues of the cerium group of rare earths is obtained. Monazite containing 60 to 70 per cent of the cerium group or other rare earths besides thorium, and 3000 tons, which is the annual consumption of monazite, gives about 1000 tons of cerium and about 1200 tons of a mixture of the rare earths lanthanum, neodymium, and praseodymium oxides. Considerable research work has been done in order to utilise these waste materials, and experiments have been made with almost every one of them. In order to obtain and separate the rare-earth elements thousands of crystallisations and fractionations are necessary, although cerium itself is separated with comparative ease. The untiring work carried on in the research laboratories of the industries as well as by the scientists in both America and in Europe will no doubt in time be crowned with successful technical applications of the by-products.

The monazite resources are given by Kithil as follows:—

It is difficult to give even a rough estimate of the quantities of monazite obtainable in the various countries. From close calculations, however, it is estimated that the lands in the marinhas along the seacoast of Brazil may yield from 15,000 to 20,000 tons of pure monazite. This does not include coast lands, where the deposits have been formed in comparatively short time.

In the interior of Brazil the writer knows of about 18,000,000 of monazite-bearing gravel deposits, which should yield monazite containing $4\frac{1}{2}$ per cent of thorium oxide, and it can be estimated that these gravels contain 45,000 to 60,000 tons of monazite. No doubt there will be found many other deposits of greater or less extent in the interior of Brazil, but no single deposit in the interior, so far as known, would warrant the erection of a large plant. In sections where several large deposits are found together or near each other a washing and concentrating plant might be profitably established, provided the price for the monazite obtained were higher than at present (May, 1915), and especially if transportation facilities from the interior to the coast become better.

The amount of purified monazite available in the Carolinas may be conservatively estimated at about 15,000 to 20,000 tons ($4\frac{1}{2}$ per cent ThO_2).

With better methods of mining and refining perhaps

these deposits could be profitably exploited at the present prices for monazite and thorium nitrate, especially if the mining of monazite were carried on in connection with the manufacture of thorium nitrate and mesothorium.

It is known that attempts have been made to extract the monazite from the native rock, but this operation with even the richest rock known—0.1 to 0.2 per cent of monazite—has proved too expensive.

Duty on Monazite Exported from United States and Brazil.—There is no duty on monazite exported from the United States.

The duties on monazite exported from Brazil vary greatly, and are as follows:—

Federal Government.—Duty on monazite from the marinhas (situated along the entire coast and navigable rivers of Brazil) is charged at the rate of 50 per cent ad valorem, and is fixed at £30, or about 150 dols. per ton. Individual States have fixed duties as follows:—

Rio de Janeiro.—Approximately 21 dols. per metric ton.

Espírito Santo.—80 per cent of selling value, established to be £25 per ton. This duty is varying, and is subject to reduction when applied for.

Minas Geraes.—12 per cent ad valorem, fixed at £25 per ton and 25 per cent ad valorem, fixed at £25 per ton, plus £2 specific duty.

Imported Duties.—The duty on monazite imported into the United States has been 6 cents per lb., but was reduced to 4 cents in 1910, and is now 25 per cent ad valorem.

The import duty on mantle ashes is 10 dols. ad valorem.

The import duty on nitrates has been 25 per cent ad valorem.

The Tariff.

In view of the increased price of thorium, the *American Gas Light Journal* has obtained expressions from several of the large users of thorium regarding changes in the tariff that would forestall any increase in the retail price of the gas mantles.

The opinion seems to be general that as long as the American mantle-makers can obtain monazite sand from abroad the prospects of using American deposits are doubtful. On the other hand, a reduction in the tariff on sand and an increased duty on the finished mantle would do much to stabilise the industry. As an incentive to American manufacturers the duty is hardly scientific, as it calls for 25 per cent ad valorem on sand, thorium, and on mantles.

If we are to be protected from wholesale dumpings the rates could better be arranged with free ore, 25 per cent duty on thorium, and 40 per cent duty on mantles.—*Chemical Engineer*, xxii., No. 6.

THE CHEMICAL ACTIVITY OF THE IONS OF HYDROCHLORIC ACID DETERMINED BY ELECTROMOTIVE FORCE MEASUREMENTS.

By JAMES H. ELLIS, Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

THE fact that the laws of perfect solutions which are conformed to by unionised or slightly ionised substances in dilute aqueous solutions are subject to large deviations in the case of largely ionised substances (salts, strong acids, and bases) even at small concentrations makes it necessary, in the absence of any theoretical explanation of the deviations, to treat dilute solutions of these substances like concentrated solutions of other substances, namely, to determine experimentally the behaviour of the separate substances, with the hope that this empirical study may then lead to generalisations. Now, the most important characteristic of ionising substances is the chemical activity which results from their ionisation, or more

specifically the (mass-action) effect which their ions exercise in determining chemical equilibria. This effect in the case of theoretically perfect solutes is proportional to the concentration of the ions; but in the case of deviating solutes there must be substituted for it a new quantity, which may be regarded as the "effective ion-concentration," and which has been appropriately called by Lewis the activity of the ions (*Proc. Am. Acad.*, 1907, xliii., 259; *Zeit. Phys. Chem.*, 1908, lxi., 129). This quantity has been shown by Lewis to be thermodynamically related to various other properties of solutions, thereby on the one hand increasing its practical significance, and on the other affording independent means of evaluating it.

The most general of these thermodynamic relations, one indeed which may well be regarded as the best practical definition of activity, is that afforded by the equation $F_1 - F_2 = RT \log (a_1/a_2)$ in which R is the perfect-gas constant and $F_1 - F_2$ represents the decrease in the free-energy of the system attending the transfer at the absolute temperature T of one molecule of any substance (thus of an ion) from a solution of any concentration, in which its activity is a_1 to another solution of any concentration in which its activity is a_2 ; the free-energy decrease being defined, in general, to be equal to the maximum work W producible by the change in the state of the system under consideration diminished by the attendant increase in the product of its volume and pressure; that is $F_1 - F_2 = W - (p_2v_2 - p_1v_1)$.

The most direct way of determining the free-energy decrease attending the transfer of ions from one concentration to another, and thereby of determining their relative activities, is the measurement of the electromotive force of cells in which such a transfer takes place, and it is with such a study of the ions of hydrochloric acid that this investigation deals. Namely, measurements have been made of the electromotive force at 18, 25, and 35° of cells of the form H_2 (1 atm.), HCl (at various concentrations), Hg_2Cl_2 (solid) + Hg . If two such cells are considered to be placed in series in opposition to each other, the changes at the electrodes of the two cells compensate each other, and the net change in state when one Faraday (F coulombs) of electricity passes through it is the transfer of 1 HCl or of 1 H^+ and 1 Cl^- from one solution to the other. Considering the ions, we have therefore the relation $(E_2 - E_1)F = F_1 - F_2 = 2RT \log (a_1/a_2)$, in which $E_2 - E_1$ is the difference in the electromotive force of two cells in which the acid has the free-energies F_2 and F_1 and its ions have the activities a_2 and a_1 , respectively. For a_2 and a_1 we may substitute a_2c_2 and a_1c_1 , in which a_2 and a_1 are activity coefficients (analogous to ionisation coefficients) representing the factors by which the concentrations c_2 and c_1 of the acid must be multiplied to give the activities of the ions.

The mean corrected values of the observed electromotive force in volts and the values of the free-energy decrease in joules calculated from them by the equation $F_1 - F_2 = 96500 E \times 4.182$ are given in Table I. These electromotive forces are probably not in error in any case by as much as 0.1 millivolt. The free-energy decrease is that attending the cell reaction $\frac{1}{2}H_2$ (1 atm.) + $\frac{1}{2}Hg_2Cl_2$ (solid) = Hg (liquid) + $H + Cl^-$ (at concentration c). The table also contains the values of the increase $(H_2 - H_1)$ in the heat content of the cell when this reaction takes place at 25°, calculated by the fundamental thermodynamic equation:—

$$\frac{H_2 - H_1}{T} dT = d\left(\frac{F_1 - F_2}{T}\right).$$

In Table II. are given the corresponding values of the free energy of transfer and heat of transfer of 1 HCl from solutions of various concentrations to a solution of the concentration 0.1000 mols. HCl per 1000 grms. water. These are obtained from the values of Table I. by direct subtraction (after reducing the values at the concentration 0.1004 so as to correspond to the round concentration 0.1000). In the table are included also values of the

TABLE I.—Energy-effects Relating to the Reaction $\frac{1}{2}\text{H}_2(1 \text{ atm.}) + \frac{1}{2}\text{Hg}_2\text{Cl}_2 = \text{Hg} + \text{HCl}$ (at various Concentrations).

Mols. HCl r 1000 grms. water.	Electromotive force at—			Free energy decrease at—			Heat decrease at 25°.
	18°.	25°.	35°.	18°.	25°.	35°.	
4.484	0.15759	0.15506	0.15124	15208	14964	14595	25590
1.9278	0.23763	0.23589	0.23304	22937	22764	22489	31483
1.0381	0.27919	0.27802	0.27595	26942	26829	26629	32130
0.7714	0.29654	0.29571	0.29411	28616	28536	28381	32450
0.595	0.31912	0.31865	0.31765	30795	30750	30654	33070
0.3376	0.33845	0.33836	0.33794	32661	32652	32611	33383
0.1004	0.39764	0.39884	0.4013	38373	38489	38612	34060
0.0333	0.45020	0.45258	0.45557	43444	43674	43963	34370

TABLE II.—Energy-effects attending the Transfer of Hydrochloric Acid and Value of its Activity Coefficient.

Mols. HCl per 1000 grms. water.	Free energy decrease at—			Heat decrease at 25°.	Activity- coefficient at 18°.	Conductance- ratio at 18°.
	18°.	25°.	35°.			
4.484	23184	23544	24037	8474	2.23	—
1.9278	15454	15744	16143	3591	1.063	—
1.0381	11449	11679	12003	1937	0.864	0.841
0.7714	9775	9971	10250	1619	0.823	0.868
0.595	7596	7757	7978	999	0.795	0.889
0.3376	5730	5856	6021	684	0.816	0.901
0.1000	0	0	0	0	0.844	0.925
0.0332	-5053	-5167	-5331	-300	0.892	0.955
0.01668	-8224	—	—	—	0.926	0.966
0.01115	-10084	—	—	—	0.943	0.971
0.008324	-11447	—	—	—	0.953	0.976
0.006683	-12472	—	—	—	0.960	0.978
0.005569	-13325	—	—	—	0.967	0.980
0.003334	-15717	—	—	—	0.985	0.985
0.001667	-19031	—	—	—	0.988	0.988

free energy of transfer at 18° for concentrations below 0.0333 molal, these having been calculated from Jahn's measurements of the electromotive force of concentration cells of the type $\text{Ag} + \text{AgCl}, \text{HCl}(c_1), \text{HCl}(c_2), \text{AgCl} + \text{Ag}$ (*Zeit. Phys. Chem.*, 1900, xxxiii., 545). In the next to last column of the table are given the corresponding values of the activity coefficients at 18°, calculated by the equation given above on the assumption that at the smallest concentration (0.00167 molal.) the activity coefficient is equal to the ionisation coefficient (0.988) derived from the ratio of the equivalent conductance at that concentration to that extrapolated for zero concentration. The last column of the table gives the values of this conductance ratio at 18° at the other concentrations, enabling a comparison of it to be made with the values of the activity coefficient.

It will be seen from Table II. that with increasing concentration the activity coefficient first falls more rapidly than the conductance ratio, being about 10 per cent smaller than the latter at concentrations 0.1 to 0.5 molal. This shows that at these concentrations there is an error of this magnitude in the common practice of employing in mass-action expressions the conductance ratio as a measure of the activity of the ions of the acid. The activity coefficient, moreover, unlike the conductance ratio, passes through a minimum at about 0.50 molal., and then increases rapidly with the concentration, becoming about equal to that ratio at 1 molal., and attaining at 4.5 molal. a value two and a quarter times as great as that at zero concentration. This large increase is in correspondence with the rapid increase of the vapour pressure of the acid at high concentrations.

Other exact electromotive force investigations from which ion activities can be derived have been published by Jahn (*loc. cit.*) on potassium chloride and sodium chloride at concentrations between 0.00167 and 0.033 molal., and by MacInnes and Parker on potassium chloride between 0.001 and 0.5 molal. (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1445). The results of the last-named investigators give for the activity coefficient of potassium chloride the values 0.653 at 0.5 molal., 0.738 at 0.1 molal., and 0.885 at 0.01 molal. The corresponding values for hydrochloric acid presented in this article are 0.795, 0.844, and 0.945.

The value (0.738) for potassium chloride at 0.1 molal. is again much smaller (namely, about 14 per cent smaller) than the conductance ratio (0.861).

A more complete description of this research will soon appear in the *Journal of the American Chemical Society*. The preparation of the cells so as to secure constancy and reproducibility of the electromotive force values, the methods of making the measurements, the full experimental data, the thermodynamic calculations from them of other free energy values will be there presented in detail.

This research has been carried on with the co-operation of Prof. A. A. Noyes, and with the aid of a grant made to him by the Carnegie Institution of Washington. The preliminary experiments were made jointly with Dr. Louis Weisberg, and the final measurements with Mr. Frank W. Hall. For all this assistance I wish to express my great indebtedness.—*Proceedings of the National Academy of Sciences, U.S.A.*, ii., No. 2.

THE PEPTONISATION OF CHROMIC OXIDE.

By WILDER D. BANCROFT.

FISCHER and Herz (*Zeit. Anorg. Chem.*, 1902, xxxi., 352) point out that the addition of an excess of caustic soda or potash to a green solution of chromic chloride gives rise to a clear green solution, because the precipitated hydrous chromic oxide apparently dissolves in the excess of alkali. On long standing the solution becomes cloudy through precipitation of hydrous chromic oxide. This precipitation takes place more slowly the greater the excess of alkali. It takes place more rapidly the higher the temperature. These facts, together with the difficulty of redissolving the chromic oxide in alkali caused Fischer and Herz to suspect that the apparent dissolving of chromic oxide in caustic alkali was really a peptonisation. On that assumption no alkaline chromite is formed.

Fischer and Herz made dialysis experiments and conductivity experiments to confirm this hypothesis. "An alkaline solution of chromic hydroxide was prepared by adding an excess of caustic soda to a chromic chloride

solution. This was dialysed against pure water, using animal bladder as a membrane. All the experiments showed that the water outside soon became alkaline but remained colourless for several days. A heavy precipitate of chromic hydroxide formed on the membrane. The alkaline solution of chromic hydroxide thus behaves like a typical colloid as opposed to a similar solution of aluminium hydroxide in caustic soda which contains a true compound, the aluminium diffusing perceptibly through the membrane.

"As a further confirmation of the view that chromic hydroxide is peptonised by caustic solutions, measurements of the electrical conductance were made, the underlying idea being that the electrical conductance of a solution of chromic hydroxide in caustic soda must depend on the caustic soda if the chromic hydroxide is in colloidal suspension. The precipitation of the chromic hydroxide can only affect the conductance slightly. If a compound is formed the precipitation of the chromic hydroxide involves a decomposition of the dissolved and conducting compound, and must therefore cause a change in the conductance. Since the precipitation of chromic hydroxide from a caustic soda solution can easily be brought about by boiling the experiments were carried out in the following way:—

"To a solution of green chromic chloride sufficient caustic soda was added to dissolve the precipitate first formed. The electrical conductance of this solution was then determined. The solution was heated and the precipitated chromic hydroxide filtered off. The conductance of the filtrate was determined, and it was found that heating and filtering had not changed the conductance. . . . From these experiments it follows with great probability that a colloidal solution is formed when chromic hydroxide dissolves in caustic soda, whereas alumina forms a compound under similar conditions. Zinc hydroxide seems to be an intermediate case, being present in alkaline solutions partly as zincate and partly in colloidal form.

"If these experiments are repeated, starting with chromic sulphate solution instead of with chromic chloride solution, there seems to be complications which are probably due to the formation of chrome sulphuric acids, and which have not been studied in detail."

While Fischer and Herz are undoubtedly right in their conclusion, some details of their experiments are not above criticism. In the first place it is not correct theoretically to say that the precipitation of the hydrous chromic oxide will have no effect on the conductivity of the solution. In so far as the hydrous chromic oxide is peptonised by hydroxyl ions the adsorption of these ions must produce some change in the conductivity. When the hydrous chromic oxide precipitates it carries down with it an indefinite amount of water and of alkali, which must also have an effect. It is possible of course that the removal of the alkali is counterbalanced practically by the removal of the water, but that can only be a coincidence and cannot be true generally. What is more likely is that the change of conductivity fell within the limit of experimental error, since there was present a large excess of caustic soda. One would have felt more confidence in the unpublished data if Fischer and Herz had not obtained results which agreed admirably with their faulty theoretical conclusions. It seems desirable, therefore, to confirm their results by other experiments, and this has been done for me by Mr. Nagel (*Journ. Phys. Chem.*, 1915, xix., 621).

Fischer and Herz state that an alkaline solution of hydrous chromic oxide becomes turbid on standing owing to the precipitation of the oxide, and that this precipitation takes place more slowly the greater the excess of caustic alkali, but they do not say how great the precipitation is, apparently because they were more interested in the fact that practically complete precipitation can be obtained in a short time by heating the solution. Mr. Nagel treated freshly precipitated hydrous chromic oxide with an excess of caustic potash to prevent jelling, and set the solutions

away in glass-stoppered bottles. At the end of three weeks a large amount of green precipitate had formed, but the liquid was still green. At the end of two months the solution was only faintly yellowish green, the bulk of the chromium oxide having precipitated. There is therefore a slow agglomeration and precipitation of the peptonised oxide, the rate of agglomeration being cut down by the excess of the peptonising agent, the hydroxyl ions.

Filtration experiments have also been made, using a Bechhold ultra-filtration apparatus (*Zeit. Phys. Chem.*, 1907, lx., 257; 1908, lxiv., 328) and collodion filters. The hydrous chromic oxide is filtered out completely from an alkaline solution, the filtrate coming through colourless. While there may be some adsorption by the filter this is of no importance, because the filtration was carried on until hydrous chromic oxide was left in mass on top of the collodion filter and could be scraped off from it. Chromic chloride solution, on the other hand, runs through green, the dissolved salt not being removed.

This raised the question as to what one has in a so-called basic chromic solution. When hydrous chromic oxide is heated with a chromic chloride solution some of the chromic oxide seems to go into solution. With an ultra-filter the chromic chloride solution passes through, while the hydrous chromic oxide is filtered out. It is therefore clear that a so-called basic chromic chloride solution contains hydrous chromic oxide peptonised but not dissolved by chromic chloride. There is no evidence that any appreciable amount of basic salt is formed in solution, though no quantitative measurements have been made in regard to this.

Mr. Nagel also tried to shake out peptonised chromic oxide with benzene or kerosene, but this proved impossible in alkaline solutions. When precipitated oxide is shaken with water and benzene it goes into the dineric interface (Bancroft, *Journ. Phys. Chem.*, 1915, xix., 275), but addition of caustic alkali causes it to precipitate, presumably because the alkali is itself adsorbed by the organic liquid (Wilson, *Journ. Chem. Soc.*, 1848, i., 174; Twomey, *Journ. Phys. Chem.*, 1915, xix., 360).

Fischer and Herz (*Zeit. Anorg. Chem.*, 1902, xxxi., 355) state that an alkali chloride has very little effect in precipitating hydrous chromic oxide peptonised by caustic soda, but that it has a marked effect in precipitating hydrous chromic oxide peptonised by barium hydroxide. This is undoubtedly due to the fact that the bivalent barium ions are adsorbed more strongly than the univalent sodium ions, and consequently make the peptonised oxide more nearly neutral and less stable. I should expect to find that barium hydroxide has a lesser peptonising action than caustic soda. This experiment was not tried by Fischer and Herz, but they showed that caustic potash has a greater peptonising action than caustic soda, which proves that the concentration of hydroxyl as ion is not the sole factor in peptonisation. In line with this is the fact that hydrous chromic oxide peptonises hydrous ferric oxide and is carried down by it (Nagel, *Journ. Phys. Chem.*, 1915, xix., 331).

General Conclusions.

1. Using a collodion ultra-filter it is possible to filter out the hydrous chromic oxide peptonised by caustic alkali.
2. On long standing nearly all of the peptonised chromic oxide precipitates from a caustic alkali solution.
3. Chromic chloride solutions peptonise hydrous chromic oxide. No appreciable amount of basic chloride appears to be formed.
4. It is not possible to shake out hydrous chromic oxide from an alkaline solution either with benzene or kerosene, even though benzene will remove hydrous chromic oxide from water.
5. Since hydroxyl ions are the active peptonising agents with hydrous chromic oxide, a strongly adsorbed cation will decrease the stability of the colloidal solution.
6. The order of decreasing stability is potassium, sodium, barium, iron.—*Chemical Engineer*, xxii., No. 6.

MYSTERIES OF MATTER.*

SOME OF THE MARVELS OF THE PROPERTIES AND
CONSTITUTION OF THE ATOM.

By JOHN CANDEE DEAN.

In the study of the vast, or of the minute, the imagination is incapable of comprehending the spaces involved. When we say that the sun is more than a million times larger than the earth, the statement does not present a mental picture of the sun's magnitude. A better conception of the sun's immensity can be obtained by saying that if the earth were placed in the centre of a spherical shell, with a diameter equal to that of the sun, the moon's orbit would be a little more than half way between the earth and the shell of the sphere. But sizes of all things are relative. The magnitude of the sun is insignificant compared with some of the fixed stars. Prof. Kapteyn estimates that the red star Antares, in the heart of the Scorpion, is 3400 times as brilliant as the sun. The diameter of Antares is estimated to be 160 million miles, or nearly as great as the orbit of the earth.

We meet with the same difficulties in attempting to comprehend the spaces occupied by molecules, atoms, and electrons. Lord Kelvin said that if we could magnify a drop of water to the size of the earth, the atoms then might appear to be somewhat smaller than cricket balls. The average atom has been estimated to be 100,000 times as large as the electron. Now to bring the electron up to the size of Kelvin's magnified atoms, it would be necessary to magnify a drop of water to 100,000 times the size of the earth.

For nearly one hundred years Dalton's atom kept its place in the theory of the structure of matter. This atom was supposed to be the ultimate particle of matter, and stability was believed to be an essential characteristic of all the elements. At the beginning of the present century, the old theory of the indivisible atom, and of the stability of the elements, was upset by the discovery that certain rare elements were disintegrating, and changing, by throwing off particles much smaller than atoms. It must not be assumed that this discovery demolishes the atom. It does not. The atom continues to be the unit that enters into all chemical combinations. The hydrogen atom was formerly the smallest particle known to science. Now the smallest particle known to science is the electron, whose weight is one seventeen hundredth part of the hydrogen atom.

Herbert Spencer said, in substance, that organic progress consists in a change from the homogeneous to the heterogeneous, and this law of progress is the law of all progress. He said "From the earliest traceable cosmical changes, down to the latest results of civilisation, we shall find that the transformation of the homogeneous into the heterogeneous is that in which progress consists." No two elements have atoms of the same size or weight, and each of the different elements has strong individual characteristics. Atoms are therefore heterogeneous, and according to Spencer's law they must have been evolved from a lower stage of matter. Now electrons appear to be absolutely homogeneous, since all electrons are of the same weight or mass, carry the same electric charge, and always turn out to be the same thing, regardless of the metal that forms the negative electrode, or the gas from which they are derived. Hence, according to the Spencean law, they should be the primal substance from which matter is evolved.

Stability is no longer regarded as an essential characteristic of the elements. The element radium disintegrates by the explosion of its atoms. The primary elements subject to disintegration by atomic explosions are uranium, actinium, and thorium. Radium is derived from uranium in consequence of its throwing off three atoms of helium. Hydrogen (1.008) is the lightest of the elements. Ura-

nium is the heaviest. Its atom is 238.5 times as heavy as hydrogen. The atomic weight of helium is 4. Three atoms of helium would be 12, hence uranium (238.5) - helium (12) = radium (226.5). The atomic weight of radium is 226.4. The small difference is probably due to the loss of electrons during the change. Radium disintegrates by the breaking up of its atoms, each radium atom hurling off one atom of helium and one of niton. The change is as follows:—Radium (226.4) - helium (4) = niton (222.4). Therefore, the atomic weight of niton is 222.4.

The explosion of the atoms of radium appears to be as complete as that of a steam boiler; the whole of the atom bursts into gases. The light atoms of helium, that form, are shot into space with a velocity of more than 10,000 miles a second and the heavy residual atoms of niton acquire sufficient velocity, in consequence of the ejection of the helium, to escape and be deposited on bodies in the neighbourhood. The expelled helium atoms are called Alpha rays. There is an inexpensive little instrument, called the Spintariscope, which is arranged with a minute particle of radium in front of a zinc sulphide screen. On looking into this interesting instrument one can see the helium atoms bombarding the screen, each atom producing a minute scintillation, the hundreds of points of light making the screen sparkle like the stars in the Milky Way. The helium atoms are so minute that the bombardment of the screen could go on for hundreds of years without any sensible diminution of the particle of radium.

Radium also emits powerful Beta rays, which consist of electrons flying out with a velocity of 100,000 miles a second, capable of penetrating thin plates of metal. A third radiation, called Gamma rays, originate in the impact of the Beta rays. They are really X-rays of such strength that shadow-graphs can be made with them through eight inches of solid lead. This radiating power is an automatic property which cannot be produced artificially. Radium is a very heavy metal; heavier than gold, mercury, lead, or any material with which we are familiar. It disintegrates very slowly. Its half period of decay is 1760 years. If a gm. of radium were put away for 1760 years, only half a gm. would remain at the end of that time; in 3500 years one-fourth gm., and in 7000 years one-eighth gm. would remain. The half period of uranium is roughly estimated at seven billion years, while that of thorium, another radio-active element, at ten billion years. An attempt has been made to estimate the age of the earth from these slowly-decaying elements.

As already stated the emanation of radium is niton, an inert substance which forms no salts. Niton's half period of decay is only four days, and its emanation is changed to a new type of matter called Radium A. Each second a definite fraction of the number of atoms present break up, and the process of degeneration continues through a number of distinct unstable forms called Radium A, B, C, D, E, F. Radium F is also called Polonium, an intensely radio-active substance with an atomic weight of 210.4. By throwing off one atom of helium its weight changes to a substance with an atomic weight of 206.4, which is close to that of lead, hence it is probable that lead is the final product of the radium series. Twenty-six so-called elements are derived from the automatic breaking up of uranium, thorium, and actinium; sixteen of which are formed by throwing off of helium atoms and are therefore real elements. Ten are formed by the emission of electrons and therefore are allotropes or pseudo-elements. It is by the ejection of full-sized atoms that substances of different chemical properties and valency result. We frequently have our attention drawn to the enormous energy stored in radium and its emanations. Sir William Ramsay states that the heat which niton parts with during its disintegration is equal to 3,500,000 times the energy available by the explosion of an equal volume of detonating gas. The principal part of this energy

* *Scientific American Supplement*, 1916, No. 2094.

comes from the expulsion of helium atoms. He also says: "If radium were to evolve its stored-up energy at the same rate that gun-cotton does, we would have an undreamed of explosive, provided always that a sufficient supply of radium were forthcoming," and Sir J. J. Thomson startles us with the statement that the atomic energy stored in an ounce of chlorine, "Is about the amount of work required to keep the *Mauretania* going at full speed for a week." He further tells us that to split up an atom of one element into different kinds of atoms, would involve enormous transformations of energy, "In fact the explosion of the atoms in a few pounds of material, might be sufficient to shatter a continent."

The electromagnetic unit is an electric current of one ampere flowing for ten seconds. A sixteen candle-power, 110-volt, carbon filament, electric lamp requires a current of one-half ampere. Therefore, such a lamp consumes one electromagnetic unit in 20 seconds. The agitation produced by the crowding together of millions of swiftly passing electrons gives rise to the brilliant light of the filament. The electric energy is so concentrated in the electrons that a mass of them equivalent to a mass of *one ounce* would suffice to light 300 of these lamps to their full candle-power, night and day for a year.

In spite of the minuteness of atoms Rutherford has been able to detect the presence of a single atom of helium. He employed a partially exhausted vessel having a tiny hole, through which, by ingenious apparatus, single atoms of helium were shot. These atoms are expelled from radium with a velocity of more than 10,000 miles a second, striking and breaking up the gaseous molecules in the vessel, producing positively and negatively charged ions, which for an instant permit a current of electricity to pass. A current measuring instrument in the line records the entrance of the atom, enabling the observer to count each one as it enters.

We appear to be getting back to Franklin's single fluid theory of electricity. The electric current is believed to be a movement of negative electrons through a conductor, from the negative to the positive, instead of flowing from the positive to the negative, as was formerly supposed. Many scientists believe that negative electricity is the only kind. Positive electricity arises from a lack of electrons. For example, a positively charged helium atom is merely a helium atom that has temporarily lost two of its electrons. In theory the negative electron is not a particle negatively charged, but is in itself a negative charge. This is equivalent to saying that matter is wholly electrical. The electron enters into the structure of the atom, but is the weight of the atom due entirely to the mass of the electron? It is claimed that the electron has no mass in itself. Its apparent weight is due to the adhering ether which it drags along, as it shoots through space. It is like stirring a bucket of water with a cane, a small quantity of the fluid will temporarily adhere to the cane and be carried along with it.

(To be continued).

PROCEEDINGS OF SOCIETIES.

INSTITUTE OF CHEMISTRY.

SPEAKING at the Thirty-eighth Annual General Meeting of the Institute of Chemistry, held at Russell Square on March 1, 1916, Sir JAMES DOBBIE, the President, referred briefly to the work of the Institute during the war and the importance of the services of professional chemists to the nation, particularly in the production of munitions and other material of war. The Institute had fulfilled a useful function, which he knew was fully appreciated by the authorities. Both in the interests of the profession and of the industries of the country the Institute had encouraged by every means possible the production of laboratory requirements of all kinds, hitherto obtained almost entirely from Germany and Austria.

In co-operation with the Society of Public Analysts steps were taken to ensure supplies of satisfactory chemical reagents, and a number of British firms immediately undertook their manufacture, according to standards prescribed by a joint committee of the two Societies.

In connection with the problem of ensuring supplies of laboratory glassware and other forms of glass, the work of the Glass Research Committee of the Institute had been remarkably successful. At the end of six months' work formulæ had been produced for practically all the various kinds of glass required in chemical operations, in addition to glasses for miners' lamps, pharmaceutical ampoules, and X-ray tubes. A number of manufacturers had taken up these industries, were now able to supply immediate requirements, and there was good reason to expect that within a short while they would have completely mastered the technique involved in the production of such articles.

Sir James Dobbie appealed to the chemists to support British manufacturers who had come to their aid, for the country should be independent of foreign sources of supply of a material so indispensable as glass, and whatever might be their views on the larger question of trade policy, there could be but one opinion as to what the policy should be where those industries usually spoken of as "key industries" were concerned.

The credit for this achievement was due to Prof. Herbert Jackson, of King's College, London, assisted by Mr. Thomas R. Merton.

The work of the Committee had received the recognition of the Advisory Council on Scientific and Industrial Research, from whom grants had been received for the furtherance of investigations with a view to the determination of formulæ for other glasses required for scientific purposes, including certain forms of optical glass.

Referring to the necessity for taking adequate measures for equipping ourselves for the economical struggle which must ensue when peace is restored, he said that the discussions which had taken place on the subject revealed a wide divergence of views, both as to the cause of the unsatisfactory position in which we found ourselves and the steps required to remedy it. In chemical industries, however, it was generally agreed that the relations between chemical science and chemical manufactures should be more intimate in the future than they had been in the past. That condition could only be fulfilled if the country possessed an ample supply of highly trained chemists. He agreed with Dr. Beilby in the belief that the phenomenal development of chemical industry in Germany had resulted much more from the large command of chemists and engineers of sound professional training than from the possession of an even larger supply of research chemists of mediocre ability. That opinion should not be taken as giving the impression that the value of research was to be underrated. So far as the supply of chemists of sound professional training was concerned he thought we could face the future with some confidence, indicating the remark-

Royal Society of Arts.—*Peter Le Neve Foster Prize.*—The prize of £10 and a Silver Medal, offered under the Peter Le Neve Foster Trust by the Royal Society of Arts for an essay on "Zinc: its Production and Industrial Applications," has been awarded to Mr. J. C. Moulden, A.R.S.M., M.Inst.M.M., of Seaton Carew, county Durham. Honourable mention has also been awarded to Mr. Ernest Alfred Smith, A.R.S.M., M.Inst.M.M., Deputy Assay Master of the Sheffield Assay Office, for his essay. The adjudicators, on whose recommendation the award was made, reported that the two essays above mentioned were distinctly superior to the others, several of which, nevertheless, were of interest and value. An essay by Mr. Ramji Das Vaishya, of Gwalior, Central India, contained a good deal of information with regard to the production and utilisation of the metal in the East Indies. The prize essay will be read in abstract at one of the meetings of the Society after Easter.

ably increased facilities for training chemists which had been afforded in this country within his memory. It had to be admitted, however, that the great public schools were for the most part unsympathetic towards the study of science, and even when they were excellently equipped for the purpose the results were meagre and unsatisfactory.

Referring to the older universities, he thought it must be allowed that Cambridge had lately achieved an extraordinary measure of success in adapting its teaching to the needs of modern times, while the fact that Oxford was rousing herself to meet her responsibilities was shown by the terms of a memorandum issued by the Natural Sciences Board in support of a reform in the regulations for the Honours Degree in chemistry, whereby research would become a compulsory part of the curriculum. He advocated a system of general education on broad lines throughout, including both classics and science, up to the proper age for specialisation. Should they fail to answer the expectation of the country the inevitable result will be that schools established on more modern lines will gradually replace the old public schools as the training-ground of the leaders of the nation.

Sir James Dobbie intimated that the Council of the Institute were about to give further consideration to the problem of promoting a more complete organisation of professional chemistry in the interests of the industries of the country.

Referring to the position of the Institute in its relation to scientific, and more especially chemical education, he expressed the view that the list of institutions recognised by the Council for the training of candidates for the Associateship should be extended. Colleges which could train candidates satisfactorily for the degree of B.Sc. ought to be encouraged by every means to prepare candidates for professional qualifications. Further, he hoped that the Institute would, without lowering the standard of its requirements, act as an attesting rather than an examining body in the case of graduates who had secured honours in chemistry, following on a course of at least four years' systematic training.

Chemistry was a comparatively young profession, which was gradually establishing itself in the knowledge and, he hoped, the good opinion of the community. It would be successful in this in proportion as it attracted men of strong character and individuality, efficient, and capable of holding their own as professional men. As it gained in strength its services would become more widely recognised, and would meet with the same appreciation as that accorded to the older learned professions. The fact that the title chemist had long been identified in this country, alone of all European countries, with the craft of pharmacy was responsible for much of the confusion existing in the public mind, but the public were learning at present so much about the work of the chemist that he did not despair of seeing the day when it would be common knowledge that while in law all pharmacists were chemists all chemists were not pharmacists.

The Officers and Council for the ensuing year were elected as follows:—

President—Sir James Johnston Dobbie, LL.D., D.Sc., F.R.S.

Vice-Presidents—E. J. Bevan; M. O. Forster, D.Sc., F.R.S.; A. Harden, D.Sc., F.R.S.; Otto Hehner; H. Jackson; and A. Smithells, B.Sc., F.R.S.

Hon. Treasurer—A. Gordon Salamon, A.R.S.M.

Members of the Council—H. Ballantyne; R. F. Blake; R. Bodmer; W. T. Burgess; H. C. H. Candy, B.A., B.Sc.; C. F. Cross, B.Sc.; A. Findlay, M.A., D.Sc.; G. J. Fowler, D.Sc.; G. G. Henderson, M.A., D.Sc., LL.D.; W. R. E. Hodgkinson, Ph.D.; G. T. Holloway, A.R.C.S.; P. H. Kirkaldy; A. H. Knight; A. Lauder, D.Sc.; H. R. Le Sueur, D.Sc.; B. McNeill, A.R.S.M.; G. T. Morgan, D.Sc., F.R.S.; D. Northall-

Laurie; F. R. O'Shaughnessy, A.R.C.S.; P. A. Ellis Richards; W. H. Roberts, M.Sc.; R. Robertson, M.A., D.Sc.; G. Stubbs; F. Napier Sutton; W. Lincoln Sutton; Thomas Tickle, B.Sc.; and W. H. Willcox, M.D., B.Sc.

ROYAL SOCIETY.

Ordinary Meeting, February 24, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Mathematical Contributions to the Theory of Evolution. XIX. Second Supplement to a Memoir on Skew Variation." By Prof. KARL PEARSON, F.R.S.

This memoir adds certain additional types of frequency curves to those published by me in memoirs in the *Phil. Trans.* of 1895 and 1901. It sums up by aid of a diagram the old results and the present additions. It further illustrates by an important general case that frequency curves are distributed over a wide area of the β_1, β_2 plane, where β_1, β_2 are fundamental statistical constants, and that only evil can arise from inflating the Gaussian point ($\beta_1 = 0, \beta_2 = 3$) to cover the whole of this area.

The entire subject is, in the author's opinion, of much importance, as significant differences are in many branches of science determined by the so-called "probable error" of the measured quantities, whether they be means, standard deviations, or correlations. But such "probable errors" have little if any meaning if it can be shown that the sample value is not even the most probable value of the statistical constant in the sampled population, and that the samples are not distributed in a form in the least approaching the Gaussian distribution about the mean value of samples.

In every case it is needful to determine the actual frequency distribution, and in nine cases out of ten in samples such as are in common use in psychology, astronomy, or physics—what the statistician terms small samples—it is easy to demonstrate that the distribution is very far from the Gaussian type, but may be markedly skew to such an extent that the ordinary "probable error" is meaningless.

"Relative Combining Volumes of Hydrogen and Oxygen." By F. P. BURT and E. C. EDGAR.

The gases were measured successively in a constant-pressure pipette at 0° C. and 760 mm. pressure.

(i.). In the first series hydrogen and oxygen were prepared by electrolysis of barium hydroxide solution. The hydrogen was purified by passage over charcoal cooled in liquid air, the oxygen by liquefaction and fractionation. Mean value for ratio of combining volumes from twelve experiments was 2.00294.

(ii.). In a second series the hydrogen was purified by passage through the walls of a palladium tube. Mean ratio from ten experiments, 2.00292.

(iii.). In a third series (hydrogen prepared as in ii.), the oxygen was obtained by heating potassium permanganate, and after purification was liquefied and fractionated. Mean ratio from ten experiments, 2.00292.

A small constant error, affecting all three series, was discovered and measured. The estimated correction increased the mean of each series by 33 parts in a million, so that the corrected means became:—

(1) 2.00301 (2) 2.00299 (3) 2.00299

(iv.). A fourth series, in which this source of error was eliminated (the gases being made and purified as in Series iii.), gave as mean ratio from ten experiments 2.00301.

Another small constant error, affecting all four series, was discovered and measured. The estimated correction

reduced each by 6 parts in 100,000, so that the corrected means became:—

(1) 2'00289 (2) 2'00287 (3) 2'00287 (4) 2'00289

(v.). A fifth series, in which both above-mentioned sources of error were eliminated, gave mean ratio from twelve experiments, 2'00287, practically identical with final mean of first four series to which the corrections had been applied.

In all these experiments hydrogen had been in excess. Four determinations were carried out with oxygen in excess. The mean was 2'00287.

The figure 2'00288 is adopted as final value for ratio of combining volumes at 0° C. and 760 mm. pressure. This differs from the value of Scott (2'00285) by only 3 parts in 200,000.

The resulting atomic weight for hydrogen ($O = 16$) computed from Morley's value for the density ratio ($\frac{0.089873}{1.42900}$) is 1'00772, very nearly the arithmetic mean of Morley's and Nöges's values (1'00762 and 1'00787).

"Speed Effect and Recovery in Slow-Speed Alternating Stress Tests." By W. MASON.

Repeated cycles of equal direct and reverse torque have been applied to mild steel specimens of tubular form, and systematic measurements made of the range of the corresponding torsional strains. The speed of application of the cycles was varied between 2 and 200 per minute. After a considerable number of cycles at 2 per minute, the range of non-elastic strain was reduced about 50 per cent on change of speed to 200 per minute, the range of torque being unaltered.

Similarly if a specimen had endured a considerable number of cycles at 200 per minute the range of non-elastic strain was immediately increased by 50 to 75 per cent at change of speed to 2 per minute. If the latter speed was maintained the augmented range of strain decreased, quickly at first, then more and more slowly. This recovery is compared with the reduction of range of strain due to a period of rest. The author attempts to account for these variations of strain on the hypothesis of alternate production and hardening of "mobile material" in the steel.

"Ignition of Gases by Impulsive Electrical Discharge." By W. M. THORNTON.

The ignition of gases by impulsive discharge is considered first as a function of sparking distance. It is shown that the shorter the distance the greater the spark, so that the volumes of the least igniting sparks are in a typical case the same for all spark lengths. Ignition may occur with intense momentary brush discharge, generally with the true disruptive spark. The products of combustion are found to be ionised and to carry a positive charge.

The gases examined were mixtures in air of hydrogen, methane, propane, and pentane, of ethylene and acetylene, carbon monoxide and cyanogen, coal gas and a mixture of equal volumes of hydrogen and methane. Hydrogen, propane, pentane, and carbon monoxide rise gradually in difficulty as the percentage of oxygen is reduced, methane is ignited by the same spark whatever the percentage of gas may be, acetylene and cyanogen have the stepped atomic type of ignition, ethylene is more inflammable in rich mixture. Hydrogen and methane in equal volumes are ignited as methane in type, hydrogen in magnitude.

The limits of inflammability of the paraffins are shown to be reached, the upper limit when there is twice the volume of combustible gas to that in the mixture for perfect combustion, the lower limit when the volume of oxygen is twice that for perfect combustion less one atom to the molecule. The ignition of coal gas is through methane. Four types of electrical ignition are given, covering all from the most rapid to the slowest rate of discharge from the poles.

CHEMICAL SOCIETY.

Ordinary Meeting, February 3, 1916.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society through death of Messrs. Ivan Richard Gibbs (killed in action), Frank Stanley Benton, and William Drake Crumie.

Messrs. O. Colverd and E. J. Mumford were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Ernest Arthur Bearder, M.Sc., Mayfield, Sale, Cheshire; William Arthur Graham Burton, Claymer, Bushey Wood, Totley, Sheffield; Ernest John Dobbs, The Cedars, 88A, East India Road, Poplar, E.; Robert Ferguson, 54, Derringham Street, Hull; William Edward Garner, M.Sc., Wymeswold, Loughborough.

Prof. W. H. BRAGG, M.A., F.R.S., delivered a lecture entitled "The Recent Work on X-Rays and Crystals and its Bearing on Chemistry." After a discussion, in which Prof. H. E. Armstrong, Lt. Bragg, Mr. W. Barlow, and Sir William Tilden took part, a vote of thanks to the lecturer was proposed by the PRESIDENT and unanimously carried.

Ordinary Meeting, February 17, 1916.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Archibald Clark, 11, Walmer Terrace, Ibrox, Glasgow; Geoffrey Edwin Foxwell, 74, Brunswick Street, Sheffield; Edward Owen Jones, B.Sc., 3, Pentyla Aberavon, Port Talbot; Hugh Findlay MacLachlan, Denburn House, Withington, Manchester; James Baird MacLachlan, Rookwood, Broughton Park, Manchester; Arthur Marsden, Gas Company, Upper Bristol Road, Bath; Bangalore Pasupuleti Balakrishna Naidu, M.B., Ch.B., Bacteriological Laboratories, The University, Liverpool; Hubert Ernest Page, Lowland Farm, Shrewley, Warwickshire; George Humphrey Pierson, 6, Station Road, New Barnet.

THE PRESIDENT announced that the following changes in the Officers and Council were proposed by the Council:—
Vice-Presidents to retire—Prof. H. Brereton Baker and Dr. Horace T. Brown.

Ordinary Members of Council to retire—Dr. T. M. Lowry, Mr. W. Macnab, Dr. E. J. Russell, and Prof. J. M. Thomson.

As President Dr. Alexander Scott.

As Vice-Presidents who have filled the office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Prof. Harold B. Dixon, Prof. Percy F. Frankland, Dr. A. G. Vernon Harcourt, Prof. W. Odling, Prof. W. H. Perkin, Sir William Ramsay, Prof. J. Emerson Reynolds, Sir Edward Thorpe, Sir William A. Tilden.

As Treasurer—Dr. M. O. Forster.

As Honorary Secretaries—Dr. Samuel Smiles and Prof. J. C. Philip.

As Foreign Secretary—Lieut.-Col. Arthur W. Crossley.
As Vice-Presidents—Prof. P. B. Bedson, Prof. G. G. Henderson, Mr. C. T. Heycock, Prof. F. R. Japp, Prof. A. Lapworth, and Prof. R. Threlfall.

As New Ordinary Members of Council—Mr. A. Chaston Chapman, Mr. Charles A. Hill, Dr. R. H. Pickard, and Dr. F. L. Pyman.

Sir Alexander Pedler, Prof. A. Liversidge, and Dr. C. A. Keane were elected Auditors to audit the Society's Accounts.

Dr. R. W. Innes and Mr. J. A. Goodson were elected Scrutators, and a ballot for the election of Fellows was

held. The following were subsequently declared duly elected:—Ralph Hall Atkinson, B.A.; Thomas James Bandinel; Christopher Barber; Raymond Renard Butler; Charles William Carpenter, M.Sc.; Harry Dean; Niralatin Dhar; James Russell Downie; Robert Ensoll; Fred Fairbrother, B.Sc.; Robert Benjamin Forster, Ph.D.; Kakui Goto; Claude Saville Grace, B.Sc.; Frank Nettleton Harrap, M.Sc.; Ernest Mostyn Hawkins; Albert Francis Huggins; Stanley Percival Kipping; Philip Lelean, F.R.C.S., D.P.H.; Leroy Wiley McCay; Wilfred Mather; Donald John Matthews; Arthur Moore, B.Sc.; John Walter Hyde Oldham, B.A.; Reginald George Parker, B.Sc.; Arthur R. Penfold; Sidney Radcliff, B.Sc.; John Read, M.A., B.Sc., Ph.D.; John Beauchamp Salter, B.Sc.; Guy Thomas Percy Tatham, B.Sc.

The following papers were read:—

"The Simultaneous Estimation of Carbon and Bromine by the Chromic Acid Method." By W. P. ROBERTSON.

"Additive Compounds of s-Trinitrobenzene with Heterocyclic Compounds containing Nitrogen in the Ring." By S. G. SASTRY.

"The Study of Binary Mixtures. Part II. Densities and Viscosities of Mixtures containing Substituted Phenols." By A. BRAMLEY.

"The Study of Binary Mixtures. Part III. Freezing-point Curves." By A. BRAMLEY.

"The Study of Binary Mixtures. Part IV. Heats of Reaction and Specific Heats." By A. BRAMLEY.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 1, 1916.

Mr. GEORGE EMBREY, President, in the Chair.

MESSRS. Thomas John Hitchcock and Nelson Trafalgar Foley were elected members of the Society.

A certificate was read for the first time in favour of Mr. Maurice S. Salomon.

A certificate was read for the second time in favour of Mr. Frank Theodore Alpe.

The following papers were read:—

"Manufacture of Chemical Filter-paper." By E. J. BEVAN, F.I.C., and W. BACON, B.Sc., F.I.C.

The introduction deals with the taking up of the manufacture of filter-paper at the commencement of the war, with an approximation of the total consumption yearly.

The manufacture of this paper, as carried out at the present time, is practically in the hands of four firms, and from examinations that we have made from time to time such papers can be looked upon as being well up to the standard of the German makes, and in certain respects superior.

The papers are classified according to their physical characteristics, in which the main question dealt with is that of bulk. Experiments are illustrated showing the relation of this factor to the rate of filtration and absorbency tests.

The chemical side of the question, with regard to choice of material, is next dealt with, and shows the common impurities found and the methods of removing same. Organic impurities are also described, and an actual determination of such an impurity as oil is outlined.

The application of filter-paper for use in milk analysis and other work is also described.

"Pink Colour on the Surface of Margarine." By A. W. KNAPP, B.Sc., F.I.C.

Bakers of margarine left about in the laboratory often become pink on the surface. This colour is found to be due to mineral acid vapours in the air of the laboratory upon the azo colour in the margarine. As butters do not give the colour it can be used as a sorting test as follows:

—The filtered fat solidified in small beakers is placed in a crystallising dish, on the bottom of which is a filter-paper soaked in strong hydrochloric acid. The dish is covered, and the fats examined after two hours. A pink colour indicates that the sample is probably margarine. The hydrochloric acid was found to diffuse half an inch into the fat in ten days.

"A Rapid Method for the Estimation of Fat in Powders." By S. B. PHILLIPS.

The method was invented for the estimation of fat in cocoa, and is applicable to any substance which can be finely divided.

The process consists of extracting the fat from a known quantity of the substance with trichlorethylene, and of determining the fat in an aliquot part of the solution. Such a quantity of the substance as is likely to contain 1.5 to 3.5 grms. of fat is weighed by difference into a 6-ounce wide-mouthed stoppered bottle (about $3\frac{1}{2}$ inches high to the shoulder), 100 cc. of solvent at room temperature is added from a pipette, and the mixture is thoroughly shaken. The filter used is made by folding two filter-papers 9 cm. diameter together into the shape of a Soxhlet thimble, and tying them into a small perforated cork (hole about $\frac{1}{4}$ inch), which is then fixed on to the end of a 20 cc. pipette. Filtration is hastened by pressure applied to the bottle by means of a tube passed through a bung, which also carries the pipette. In this way 20 cc. of clear solution is removed, and the fat in it is determined on evaporation of the solvent. The total weight of fat in the substance taken is determined by multiplying by a factor, which varies according to the weight of fat obtained. Thus, if 0.3 gm. is obtained, the factor is 5.04; if 0.5 gm., 5.11; if 0.7 gm., 5.165.

"A New Colour Reaction for Aloes." By C. E. STACY.
A pink coloration sufficiently delicate to detect one part of Barbadoes aloes in 10,000 is produced by the addition of a freshly prepared solution of potassium ferricyanide to the cold aqueous solution of the aloes under the conditions named.

By the difference in colour of the reaction the author claims to be able to distinguish certain different varieties of aloes used in medicine from each other, and from commercial aloin in medicinal preparations.

CORRESPONDENCE.

SIMPLE FOOD TESTS.

To the Editor of the Chemical News.

SIR,—Having read in the CHEMICAL NEWS (1916, cxlii., 92) an article headed as above, and recalling having read either the same or a very similar article in an illustrated monthly magazine recently, I beg the space to make a few comments on the same. In the first case the writer of the article states that pure butter can be differentiated from margarine, or a process butter by heating a small sample in a tiny tube at a sufficient heat to melt it, this being maintained for half-an-hour, when, in the case of pure butter, the contents will be clear, whereas a certain cloudiness will be shown in the case of margarine. I have handled a good many samples of pure butter which would not answer this test, which depends upon the separation of the water and fat, and which varies considerably with the amount of churning the sample has received. The spoon test to my mind is just as unreliable, a butter cracking on boiling just as much as a margarine, especially if the butter contains, as it often does, a small percentage of salt. Any fat churned with water will crackle on heating sufficient to drive off the water. In the next case we are told that if an almost saturated solution of sugar is made in a tube and this held in front of some print it should be possible to read the same in the case of pure

sugar, whereas any turbidness will almost certainly indicate adulteration. The writer covers himself by saying that a brown or raw sugar might give a certain amount of discoloration to the water. Although handling tons of raw cane-sugar weekly I should like to say I have never met one yet which will make a clear solution with water. Also at the present time quite a lot of the sugar offered for sale in grocers' shops is not refined, but simply the raw sugar, or the raw sugar washed in the centrifugal to remove most of the dark colour and molasses, thus producing a much lighter sugar; this also does not give a very clear solution with water. In neither case does this turbidity necessarily mean adulteration. Again, we are told an unscrupulous baker will work into his bread as much salt as possible, the idea being that a loaf loaded with salt will retain more moisture and therefore weigh more. I think the salt is more often added in the case of a weak flour to toughen up the gluten and so give shape to the loaf. To tell us to judge the real value of our bread from the heaviest dry weights obtained from two or more samples is also hardly fair, varying as it will with the newness or staleness of different bakers' loaves. I quite agree that now under the present condition of trade more than at any other time should a careful watch be kept over foodstuffs and raw materials, but let the tests given, simple or complex, be reliable and not vague and inconclusive, which, if so, may condemn both the manufacturer and retailer alike.—I am, &c.,

A. B. BRADLEY.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xvii.-xviii., No. 23-24, 1915.

Electrolysis of an Aqueous Solution of Potassium Orthosulpho-antimonite, and the Composition of this Compound.—J. A. Muller.—The author has studied the electrolysis of potassium orthosulpho-antimonite, $\text{Sb}_2\text{S}_3\text{K}_3$, in two series of experiments. In the first the anode and cathode were both immersed in a solution of the sulpho-antimonite, while in the second series the cathode was immersed in the solution, while the anode was placed in a 17 per cent solution of soda separated from the antimonite solution by a porous diaphragm. The cathode was a bar of antimony and the anode a cylinder of platinum. The system was kept in an atmosphere of hydrogen to avoid oxidation. The experiments of the second series, which were the more instructive, show that during electrolysis there is no passage of negative ions containing potassium from the cathode to the anode cell. On the contrary, a certain amount of the group SbS_3 does pass from the cathode to the anode. The experiments appear to show that potassium orthosulpho-antimonite is a compound of the radical SbS_3 and three atoms of potassium, and not a compound of three negative SK groups with an atom of antimony.

Method of Preparation of Mercurised Aromatic Alcohols.—V. Grignard and A. Abelman.—Dimroth has shown that in many compounds of the aromatic series it is possible to replace directly an atom of hydrogen by the radical HgX , X being a halogen, a hydroxyl, or a monovalent acid residue. This operation, which the author calls mercurisation, can be carried out with mercuric oxide, or chloride or acetate. In the aromatic series the hydrocarbons, phenols, amines, acids, sulpho acids, ketones, &c., have been mercurised, and mercurisation is a general operation resembling nitration, sulfonation, &c. Up to the present, however, one function has proved resistant, and that is the aromatic alcoholic function. By

the action of the bromide of ethyl magnesium upon the mercurised ketones the authors have succeeded in effecting this mercurisation by observing the following precautions:—(i.). The mercurised ketones must be used in the solid state. (ii.). Only the theoretical quantity of the magnesium reagent must be employed, to avoid the reaction on the group HgCl . (iii.). The operations must always be carried out with very small quantities.

Partial Synthesis of Eserine and Geneserine.—Max Polonovski and Ch. Nitzberg.—In order to synthesise eserine the authors first tried heating eseroline with methyl isocyanate in a sealed tube without success. When the two substances reacted in the cold, molecule for molecule, a new compound was obtained, but not eserine. The authors then tried the effect of introducing traces of sodium, and they found that when CH_3CNO is heated in benzene with eseroline in a sealed tube, and in presence of traces of sodium, the product is synthetic eserine. Thus when a single molecule of CH_3CNO acts on a molecule of eseroline, according as pure eseroline or a specimen containing traces of sodium is used, the methyl-carbaminic group can be fixed on the OH or the N of the eseroline, and an addition product is thus obtained which is either a urethane (eserine) or a urea (isoeserine). Geneseroline in similar conditions yields only geneserine, giving neither an addition product nor a ureic substance preserving a phenol function. This difference of behaviour indicates that geneseroline does not possess the imide group which exists in eseroline.

MISCELLANEOUS.

Circle of Scientific, Technical, and Trade Journalists.—A Discussion on "The Sphere of the Scientific and Technical Press in Relation to Technical Education and Industrial Research" will take place at the next meeting of the Circle, to be held at 8 p.m. on Tuesday, March 14, in the Hall of the Institute of Journalists, Tudor Street, Blackfriars, London, E.C. The Chairman of the Circle (Mr. L. Gaster) will preside. Dr. William Garnett (late Educational Adviser to the L.C.C.) will open the Discussion by an introductory paper.

Faraday Society.—On Wednesday, March 15, at 8 p.m., the Society will hold an informal Discussion on "Methods and Appliances for the Attainment of High Temperatures in the Laboratory," at the Institution of Electrical Engineers, Victoria Embankment, W.C. Dr. J. A. Harker, F.R.S., of the National Physical Laboratory, will open the discussion, over which Sir Robert Hadfield, F.R.S., the President of the Society, will preside. Workers interested in the subject, and particularly those prepared to speak on the results of their personal experiences, are invited to be present and take part in the Discussion. Further particulars may be obtained from Mr. F. S. SPIERS, Secretary to the Society, 82, Victoria Street, London, S.W.

MEETINGS FOR THE WEEK.

- TUESDAY, 14th.—Royal Institution, 3. "Sea Power as a Factor in the Evolution of Modern Races," by Prof. Arthur Keith.
WEDNESDAY, 15th.—Royal Society of Arts, 4.30. "Forestry and the War," by E. P. Stebbings.
— Faraday Society, 8. Informal Discussion on "Methods and Appliances for the Attainment of High Temperatures in the Laboratory."
THURSDAY, 16th.—Royal Institution, 3. "Organic Chemistry in War—Organic Products used as Propulsive and Explosive Agents," by Prof. H. E. Armstrong.
— Chemical, S. "Molecular Association," by W. R. Innes. "Influence of Iron Pyrites on the Oxidation of Coal," by T. J. Drakeley. "Essential Oil of *Cinnamomum Oliveri* (Bail) or Brisbane Sassafras," by G. W. Hargreaves.
FRIDAY, 17th.—Royal Institution, 5.30. "The Search for New Coal Fields in England," by Dr. Aubrey Strahan.
SATURDAY, 18th.—Royal Institution, 3. "Radiations from Atoms and Electrons," by Sir J. J. Thomson.

THE CHEMICAL NEWS.

Vol. CXIII., No. 2938.

PURSUIT OF CHEMISTRY IN BENGAL.*

By PRAFULLA CHANDRA RAY, C.I.E., D.Sc., Ph.D.,
Professor of Chemistry, Presidency College, Calcutta; Dean of the
Faculty of Science, University of Calcutta.

MODERN chemistry, by which I mean scientific chemistry, is only of yesterday's origin. It may be said to date from the time of Lavoisier, who, as you all know, was one of the earliest victims of the fanatical outburst which followed in the wake of the French Revolution. In England just a century ago Dalton and Davy were in the zenith of their fame. Germany, such as we now understand by the term, did not exist at all at this time as a political entity; it was composed of Prussia and a number of petty States warring against each other and all crushed in turn under the heels of Napoleon. The two great chemists, Liebig and Wöhler, who were destined in after life to be the makers of modern German chemical greatness, were then mere lads. But in France the state of things was altogether different. The impetus given by Lavoisier's doctrine had spread far and wide, and a brilliant galaxy of experimenters, including Gay-Lussac, Dulong, Thenard, Ampère, Arago, and Chevreul, were almost every day opening out new spheres of investigation, but their inestimable acquisitions found no soil and could bear no fruit in unhappy Germany, where, to quote Liebig's own words, "it was a wretched time for chemistry." But in the course of two decades Liebig and Wöhler by their epoch-making discoveries almost revolutionised the views of chemists on organic chemistry; in fact one may go so far as to say that they created organic chemistry. Neither of these great apostles could, however, catch inspiration in their native land. The former went to Paris to learn at the feet of Gay-Lussac, and the latter preferred to repair to Stockholm in 1823 to be initiated by the great Swedish chemist Berzelius. The fire which these great pioneer chemists borrowed from Paris and Stockholm was rekindled with vigour on their return to Germany, and has been ever since burning with increased and dazzling brilliancy.

England, though she could boast of a Boyle, a Priestley, a Cavendish, a Dalton, and a Davy, was, however, slow to follow in the wake of the chemical renaissance in France and Germany. Up till the forties of the last century she was found lagging behind in the race. Liebig, who visited England in 1837, writing to Berzelius naively says:—"England is not the land of science; her chemists were ashamed to call themselves chemists because the apothecaries had appropriated the name." According to Sir Edward Thorpe there were not in 1837 more than a couple of dozen persons in the British Isles altogether receiving systematic instruction in practical chemistry, and even that supply was probably fully equal to the demand. There was in fact little to tempt men to take up chemistry as a means of livelihood. Teacherships were few in number, analytical chemistry as a profession hardly existed, and chemical manufacturing was done by rule of thumb, and for the most part very badly done.

Such was the state of things in the forties in England in the last century, and such is the state of things in the India of to-day so far as chemistry can offer attractions to young men as a means of livelihood. It is scarcely too much to say that 99 per cent of our university students who take up chemistry do so simply because it happens to be a branch of the Science curriculum, and they have to give it up and forget all about it as soon as they have

secured a degree. Yet in the midst of such discouraging and depressing circumstances we must cultivate our favourite science.

If we read carefully the history of the different branches of science we invariably find that they have attracted votaries in the early stages of their progress in the midst of almost insuperable difficulties. You all know that Copernicus held back the publication of his great book "On the Revolutions of the Heavenly Bodies" for thirty-six years for fear of giving offence to the all-powerful Church, that Bruno was burned at the stake for teaching the plurality of worlds, and Galileo visited with the terrors of the Inquisition for his vindication of the Copernican doctrine; nay, Roger Bacon, one of the precursors of our own science, was immured in a dingy cell of a cloister at Oxford for practising the black art, as chemistry was then called. Browning in his "Paracelsus" has delineated the wrestlings and inward longings of an ideal alchemist, who is only an honest seeker after truth, who pursues knowledge for its own sake irrespective of what it brings. Voltaire tells us that at the time of Newton's death there were not twenty readers of the "Principia" out of Britain. These great and mighty interpreters of the laws of nature cared not for name or fame, but considered themselves lucky if only they could be instrumental in giving to the world the results of their lifelong labours. Kepler had imposed upon himself years of incessant toil, including midnight vigils, in observing and recording the motions of heavenly bodies, and after embodying the results of his labours he exclaims, "I may well wait a hundred years for a reader, since God Almighty has waited six thousand years for an observer like myself."

If Europe is what she is to-day, if she is in the van or scientific progress, it is in no small measure due to the self-denying ordinances of these great heroes in science and their worthy successors.

I have been led to indulge in this digression because without a brief historical retrospect of the development of sciences in Europe much of what I am going to say will not be properly understood.

Those who intend to pursue chemistry in India must not expect to reap a rich harvest in the immediate or near future. India has been a *tabula rasa* so far as the cultivation of physical sciences is concerned for the last thousand years, or perhaps more. In Germany or in England for the last three hundred years—i.e., from the time of Paracelsus and Basil Valentine and Newton and Boyle—the lamp has been burning dimly in the early stages, but more and more brilliantly in the eighteenth and nineteenth centuries. We in the East, on the other hand, have been living in silent and ecstatic meditation. To the Hindu the material world is but an illusion, and Sankara as an exponent of the Vedanta philosophy is unsparing in his criticism and denunciation of the atomic theory as propounded in the Vaisesika philosophy, ridiculing the author of the system itself as "Kanāda," or atom-eater. No wonder M. Cousin in his "History of Philosophy," in giving an analysis of the Yoga philosophy and the Bhagavat-Gitā, which he calls a monument of the greatest price, quotes such passages as these:—"Science is superior to practice, and contemplation is superior to science; prefer contemplation to science, inaction to action, faith to works," &c., and concludes by observing that as man despising himself has not been able to take any thought for recalling the memory of his actions there is no history of man, and no chronology in India. No wonder Mill should write:—"The Hindu boys display marvellous precocity in appreciating a metaphysical proposition which would hopelessly puzzle an English lad."

Remember, gentlemen, what the transplantation of Western sciences into such a land and amidst such an environment means. Those who are pioneers in this field have no traditions to go by or follow up; they have to chalk out their own path and formulate their own schemes, and carry them out as best they may. Difficulties arise at every turn, but with faltering steps the weary pilgrim

* Calcutta University Extension Lecture, delivered January 10, 1916.

must keep marching on towards the goal, happy if he reaches it but equally happy if he perishes in the attempt.

This is the dawn of the year 1916—a memorable year: the centenary of the foundation of the old Hindu College, of which our own Presidency College is the direct and lineal descendant. I need not enter here into the merits of the bitter controversy between the Orientalists and the Anglicists, which ended in the triumph of the latter. The whirligig of time had brought on its own revenge. Raja Rammoan Ray, the maker of modern India, who was the first to resuscitate the Upanishads in Bengal and to translate some of them into English, and himself deeply imbued with the Vedanta doctrines, characterised Sanskrit learning as calculated to cause “a lamentable check to the diffusion of knowledge.” “Nor will youths be fitted,” cried this great reformer, “to be better members of society by the Vedantic doctrines which teach them to believe that all visible things have no real existence; that as father, brother, &c., have no real entity they consequently deserve no real affection, and therefore the sooner we escape from them and leave the world the better.” He therefore appealed to the then Governor-General, Lord Amherst, to discourage “such imaginary learning, and employ European gentlemen of talent and education to instruct the natives of India in mathematics, natural philosophy, chemistry, anatomy, and other useful sciences, which the natives of Europe have carried to a degree of perfection that has raised them above the inhabitants of other parts of the world.” These memorable words were uttered close upon a century ago, but they bear repetition even to-day.

In my article on the “Forty Years of Chemistry at the Presidency College,” published in the *Presidency College Magazine*, I have described the successive steps in the development of chemical teaching in Bengal, and I need not take up your time by their useless recapitulation. Suffice it to say that for the first sixty years or more the intellectual pabulum of the Bengali youths was furnished by Shakespeare and Milton, Bacon and Locke, and Hume and Gibbon. It is barely two decades since Bengal took seriously to original investigation in the fruitful field of chemistry. At my request Mr. Rasiklal Datta, one of the most devoted, assiduous, and successful of our workers, has drawn up a fairly exhaustive list of contributions by Bengali chemists. It is found on reference to it that within this time as many as 130 communications have been sent from the chemical laboratory of the Presidency College alone. The laboratory of my friend Prof. Watson is also responsible for two dozen or more papers.

Indeed, on opening the latest numbers of the journals of the chemical societies of London and America one's eyes are regaled with the sight of an increasing number of papers by our own students and pupils working in Bengal, as also at the laboratories of the Imperial College of Science and Technology, and the University College, London.

Gentlemen. I cannot here resist the temptation of alluding to an incident, the more so as my friend the Vice-Chancellor himself is mixed up in it, and I hope he will pardon me for what I am going to divulge, and will not regard it as a breach of confidence. As you all know, my friend and myself had the honour of representing our University at the Congress of Universities, held in London in 1912. On the first day of the session the main object of discussion was introduced by Principal Peterson, of McGill University, with the reading of a paper of singular merit, entitled “Interuniversity Arrangements for Post Graduate and Research Students.” I arranged with my brother-delegate, whose oratorical gifts I have always envied ever since he was my school-mate, now some forty years ago, that so far as the making of speeches was concerned he should take upon himself all the burden, leaving me a silent spectator and participator. He was, however, the first to give a go-by to this tacit understanding. “Now is our opportunity,” he exclaimed, and he modestly added that this was a subject to which a

student of science was calculated to do more justice. I hesitated and pleaded hard to be let off. My friend proved to be inexorable; he cut short my vacillation by tearing off a bit of the printed programme and putting down my name and forwarding it to the chairman (Lord Rosebery). Imagine my trepidation when in response to a summons from the chair I ascended the platform, the more so as I was preceded by so great a master of physical science as Sir J. J. Thomson. I ventured to point out that the Indian degrees, based as they are upon teaching imparted in India, are often stamped with a badge of inferiority simply because they are labelled as “Indian ware”! Speaking with some degree of confidence about my own branch, I further took the liberty to lay stress upon the fact that the contributions of our students were being hospitably received in the columns of the leading chemical journals of Europe and America, and I made bold to assert that their researches, if embodied in the shape of theses, would be readily accepted for a doctorate in a European university. A distinguished chemist, whose name I am not at liberty to disclose, on going through the published papers of Mr. Nilratan Dhar, has expressed his opinion that he would not hesitate for a moment to award him a doctorate so far as his own university is concerned. Two of our late pupils, Messrs. Bimanbehary Dey and Hemendrakumar Sengupta, who have lately returned home after winning golden opinions of their professors at the Imperial College of Science and the coveted distinction of the London D.Sc., may also be cited as instances. Messrs. Brajendranath Ghosh and Sudhamoy Ghosh, who have also just won Doctorates of the London and Edinburgh Universities respectively, on the basis of their theses have added lustre to the Dacca Laboratory. Mr. Anukulchandra Sarkar, the first Ph.D. of our university in chemistry, has amply proved that travelling abroad is by no means a *sine qua non* for completing one's chemical education. Mr. Rasiklal Datta has also preferred to be a stay-at-home worker, at least for the present; he has already about thirty published papers to his credit.

Datta's researches on the halogenation of organic compounds constitute a brilliant record, and have added materially to our knowledge of the subject. From the abstract of a paper in the *Berichte*, which has appeared in the *Journal of the Chemical Society*, 1915, we learn that the German chemist Kempf has been anticipated by Datta, whose work is all-embracing and covers a wider field.

Physical chemistry is yet in its infancy, but, thanks to the labours of Ostwald, Arrhenius, and others, it is beginning to assert itself. To Mr. Nilratan Dhar, one of the most brilliant amongst our late pupils, belongs the credit of initiating work in this branch in our country, and it is gratifying to note that a monograph on complexions recently published in England quotes him as an authority. Messrs. Jnanchandra Ghosh and Jnanendranath Mukherji are also devoted labourers in this field; the former is carrying on investigations on electrolysis by alternating current and the latter has taken up the fascinating subject of colloids. Their researches are being regularly published in the *Journal of the American Chemical Society*. Mr. Rajendranath De has shown in connection with his work on the molecular volumes of the hyponitrites that he has the making of a chemist in him. Nor should I omit to mention the name of Mr. Jitendranath Rakshit. As some of you may be aware, he was associated with me in the research on the isolation of the amine nitrites. Rakshit's papers on “The Sodium Derivatives of Acid Amides” show fertility of resources and marked originality. He has been receiving a grant from the Research Fund of the Chemical Society to enable him to continue the work. Mr. P. K. Dutt, also an old pupil of ours, has taken the M.Sc. degree of the University of Leeds on the strength of his thesis, I understand, on “The Progressive Bromination of Toluene.” Mr. Dutt is now engaged in research work there in connection with the manufacture of explosives. The mention of Leeds raises in my

mind pleasant associations. The chief town of York has often been a place of pilgrimage for our advanced students, and Professors Cohen, Green, and Smithells have always been ready there with their welcome and genial hospitality.

I need not proceed further. What has been said above will suffice to prove that physical science, though an exotic plant, has, like the potato, taken kindly to the soil of Bengal. Four centuries ago Vāsudeva Śārabhauma and his illustrious pupil Raghunatha Siro-nani founded the famous school of *Navya Nyaya* (Modern Logic) at Navadvīpa, whose *tohs* even now attract pupils from distant parts of India. Paradoxical as it may seem, this province of ours—the land *par excellence* of scholasticism and logic-chopping—has been equally propitious for the cultivation of physical science, and to point a moral and adorn a tale I have only to refer to the brilliant record of my distinguished colleague, Prof. Bose, who has been as a beacon-light in his own department, and whose researches bid fair to be epoch-making.

Gentlemen, just thirteen years ago, in my "History of Hindu Chemistry," in the chapter devoted to the decline of scientific spirit in India, I lamented that the spirit of inquiry had died out amongst a nation naturally prone to speculation and metaphysical subtleties. Little did I dream then that in the course of a decade or so I should have to revise the estimate I then formed of the capacities of my own countrymen, and chronicle that a bright chapter is about to dawn in our life-history.

It is scarcely necessary now to enter into an elaborate *apologia* for the cultivation of our own science. Even the man in the street realises that the battles which are being daily fought and the new surprises sprung upon the wondering public in connection with this the greatest war since the creation of the world have had their rehearsals in the laboratories of chemists, nor need I allude to the part which chemistry is destined to play in the industrial development and progress of a country. You have only to read the articles, correspondence, and controversies which are going on in the columns of *Nature*. We in Bengal are lamentably backward in commercial and industrial pursuits, and have almost become a by-word of contempt and reproach to our more fortunate brethren in Bombay, which can boast of merchant princes and captains of industry. Perhaps it may be excusable in me to point out that we have an humble and unpretending object-lesson in our infant indigenous chemical undertaking; it shows, at any rate, that something can be done even in Bengal when science is wedded to industry. Some of you may be aware that the Bengal Chemical and Pharmaceutical Works had its birth and early struggles in the dark and dingy rooms of a house not far from this place, and that it started with the modest sum of Rs. 800. With the recent expansions which have already been taken in hand it will soon cover an area of twenty-four bighas (eight acres), and its present capital of five lacs will have to be doubled with a view to the installation of new plants. It has always been a fixed principle with the directors of this business not to take in anyone as a chemist whose knowledge is not up to the M.Sc. standard of our university. There is another matter, rather of a delicate nature, which may not be passed over in silence. The works has been conceived, initiated, and managed solely by Bengali brains, energy, and pluck, and it has never been necessary to call in the aid of any foreign experts. Perhaps you may be interested to know that owing to the serious dislocation in the chemical trade due to the war and the stoppage of supplies from Germany it has been doing a roaring business in some lines; *e.g.*, magnesium sulphate is being turned out by tons and a consignment has been shipped to England; it has also been its privilege to be of some little help to Government in the matter of supply of acids, &c., for munitions. If I have at all referred to this chemical works in my address it is only to demonstrate that the successful application of science to industry is by no means incompatible with Bengali genius.

I have always been reluctant to appeal to the sordid instincts of man in giving a stimulus to the cultivation of science. I prefer that we should take our stand on a higher platform. The heroes of science, some of whose names should have been mentioned in the earlier part of my address, have always pursued their favourite branches with a singleness of purpose and without an eye to material gains, and neither penury nor persecution could damp their labour, and they have left priceless legacies as the common heritage of mankind. As a new light flashes across the mind of the inquirer, as he hits upon a novel discovery, which has made him lose his sleep and appetite for days and months, he is seized with ineffable joy often bordering upon delirium, and, unconscious of all that is around him, is led to exclaim Eureka! The vocation of a student of science is sacred; he is a citizen of the world—he transcends all artificial barriers of race and nationality.

In a country like India, where the ignorance and illiteracy of the mass of the people are simply appalling, and where every natural phenomenon, from the eclipse of the moon to the breaking out of a plague, is apt to be ascribed to providential interference or divine wrath, the cultivation of the physical sciences is of special importance. Buckle somewhat aptly observes that a nation perfectly ignorant of physical laws will refer to supernatural causes all the phenomena by which it is surrounded, and that, other things being equal, the superstition of a nation must always bear an exact proportion to the extent of its physical knowledge. The late Lord Salisbury, who, if I mistake not, was an amateur chemist, and who used to seek solace and relaxation from his busy political life in his private laboratory, observed on a memorable occasion that "even from the social point of view chemistry has undoubtedly this claim—that it is one of the most powerful agents that has moved the world; that the application of a science of that kind to the national mind by constant familiarity with its teachings, by constant knowledge of its achievements, is of the highest human value. It teaches the mind the immortal difference between guessing and knowing. And the farther chemistry goes on and the more it asserts the superiority of its ways and canons in all departments of human thought, so far shall we drive guessing to a distance and be satisfied with nothing but what we can know."

Modern India's contribution to the world's stock of scientific knowledge is almost nil: only the first sod has been turned. What little has been done represents only the feeble individual attempts of a limited number of stray workers scattered at isolated centres. There is only a hopeful indication that the spirit of research is abroad. We have unfortunately no guarantee, and as yet no provision has been made that the continuity of the work begun will be kept up. In science we are almost three centuries behind the European nations, and we have to make up for the lost ground. It should not be left to the chance, or haphazard caprice, or convenience of a solitary worker here or there, whose exit from the scene by death or retirement may spell the extinction of the spirit of research thus awakened. Moreover, the average professor in an affiliated college is an overworked man. The head of the institution, Shylock-like, exacts from him the drudgery of the routine work, and it is only by sacrificing the holidays that he can expect to do some work, and there is, after all, but one single properly equipped college, with very limited accommodation, which is affiliated to the university up to the M.Sc. standard. Every year the gates of scientific learning are cruelly barred against scores of eager aspirants knocking for admission. Add to this that there is but a single Government Research Scholarship in science annually available to the advanced student. When all these circumstances are taken into consideration the wonder is that so much has been done with so little help and such meagre materials. Surely a state of things like this is not creditable to Bengal (in-

cluding of course Behar and Orissa), with a population of eighty millions. A vast amount of potential research talent is lying unutilised and running to sheer waste. It is for these reasons that I have always looked upon the University College of Science as the materialisation of a dream of my life. Here the professors, relieved from the tedium of routine work, will have ample time at their disposal to devote to post-graduate teaching, but their main function will be to undertake and teach *research*. And the several departments working in healthy emulation and co-operation will create a scientific atmosphere. The pious founders of the endowments have with commendable foresight taken care to make ample provision for fellowships and scholarships, which will be bestowed only upon such advanced students as have already given proof of their capacity for undertaking original investigation. It would be idle to disguise the unpalatable fact that unless the Palit and Ghosh endowments are adequately supplemented the Science College will not be in a position to start fully on its active career. I hope Bengal has not seen the last of her great benefactors to our university. I trust another Palit or Ghosh will open his pursestrings in this hour of our dire need. I plead to our Government, which has done so much in the past for the progress of education, to come forward with a liberal grant.

Gentlemen, I am afraid I have already exhausted your patience. One word more and I have done. I spoke of physical science as an exotic plant in India. Perhaps I should modify or qualify the expression. Ancient India was the cradle of mathematical and chemical sciences, and I have narrated in my "History of Hindu Chemistry" how these filtered to Europe through the medium of the Arabs. Indeed, the first Faraday lecturer of the Chemical Society in the introductory part of his lecture observes:—"What an awakening for Europe! After two thousand years she found herself again in the position to which she had been raised by the profound intellect of India and the genius of Greece." Remember it is to India that the place of honour has been thus assigned by the illustrious French chemist, Jean Baptiste Andre Dumas. I hope it will be hers once more to hold aloft the torch of science and assert her true place in the comity of nations.

MYSTERIES OF MATTER.*

SOME OF THE MARVELS OF THE PROPERTIES AND
CONSTITUTION OF THE ATOM.

By JOHN CANDEE DEAN.

(Concluded from p. 116).

NATURE is more marvellous, more interesting, and more beautiful than anything that the imagination can produce. The great French astronomer and scientist Henri Poincaré tells us that the scientist does not study nature because it is useful. He studies it because it pleases him, and it pleases him because it is beautiful. He says:—"We are nature not beautiful, she would not be worth knowing, life would not be worth living. I do not mean here, of course, that beauty which impresses the senses, the beauty of qualities and appearances; not that I despise it—far from it; but that has nought to do with science; I mean that subtler beauty of the harmonious order of the parts which pure intellect appreciates."

It is a mistake to suppose that a knowledge of breaking up of atoms into smaller particles originated with the discovery of radium. As far back as 1873 Sir Norman Lockyer suggested that many difficulties of the laboratory would vanish if we conceded that atoms could be broken up into much smaller particles. In 1895 he published "Inorganic Evolution as Studied by Spectral Analysis," in which he says, "Science now has to consider masses much smaller than the atom of hydrogen." In the study of the hottest stars he found himself in the presence of furnaces of transcendental temperature shielded by their

vastness from the distracting phenomena which were present in the laboratory.

He classified the fixed stars in the order of their temperatures. Stars of the hottest class he called Argonian from the star Gamma of the constellation of Argo Navis, which has a temperature estimated by him at 50,000° F. Gamma Argus contained a set of spectral lines not before recognised, and he concluded that they indicated a new element connected with hydrogen. He called the new element proto-hydrogen, because of the relation of its lines to those of the proto-metallic lines. The Argonian stars are now called helium stars; they show but few elements. Proto hydrogen, helium, asterium, and proto-calcium are conspicuous.

Lockyer tells us that the high temperature at which proto hydrogen appears, is not the end of the simplification of stellar transcendental temperature. "The work of the dissociation of the atom carried on under our eyes in the hottest stars, is quite impossible in our laboratories." He says:—"At higher temperatures the chemical units with which we work, at low temperatures, are broken up into smaller masses, explains the spectral phenomena observed, not only in our laboratories, but in the sun and stars."—"The final breaking up by heat must be the earliest chemical forms."

Heat is a motion of the atoms of matter, and a fall of temperature slows down this motion, but man's ingenuity has not yet brought a single atom to a state of rest. The temperature of a body varies as the square of the amplitude of vibration of its atoms. If all the heat of a body could be abstracted its atoms would cease to vibrate. Increase of heat accelerates atomic motion until a critical velocity is attained that overthrows the affinities which hold the atoms in chemical combinations. At a temperature of 4000° F. the existence of water is no longer possible, not even in the form of steam. Its molecules no longer cohere, because of their energetic motion, and they dissociate into hydrogen and oxygen gases.

The heat of the sun is probably sufficient to dissociate all chemical combinations, consequently interior solar matter is in its monatomic or elementary condition, and much of it may be in the electronic state. Perhaps there is a critical or maximum temperature for all matter, where the violence of the motion of clashing atoms causes them to break up into electrons. In stars of the highest temperature, like Gamma Argus, or Zeta Puppis, the critical state has probably been reached, and the greater part of their matter is in the form of electrons. When matter is in its hottest state it is at its lowest point in the scale of evolution, and progress depends on a fall of temperature by radiation. Lockyer's inorganic evolution, joined to the nebular hypothesis, and this to geological and biological evolution, completes the evolutionary cycle of matter to its present terrestrial stage.

We now come to the most interesting, most marvellous mystery of matter. There has been collected a wealth of evidence which proves that the atom is an organised planetary system of dazzling complexity, in which electrons simulate the movements of the planets of our solar system. The negative electrons of the atom swing around the positive nucleus, like planets around the sun. The planet Neptune requires 165 years for a single revolution around the sun, but it has not made a half revolution since its discovery, while the electrons of the atom complete their revolutions around their central nucleus in a millionth or a billionth of a second. The electrons revolve in a series of concentric orbits all in the same plane. While the larger part of the mass appears to reside in the nucleus, the nucleus is relatively minute, with a diameter of probably less than 1/5000 of that of an atom. It is thought that the simpler atoms, such as hydrogen, helium, and proto-fluorine, where the electrons are few, all revolve in one ring, but in the heavier and more complex atoms their orbits lie in three to five, or more rings. The atom is as much a machine as an electric motor, and both are electro-magnetic engines.

* Scientific American Supplement, 1916, No. 2094.

Nearly the whole mass of the atom resides in the nucleus, but the nucleus is relatively very minute. It is quite impossible to imagine the extreme density of the nuclei. If an oxygen nucleus could be enlarged to a diameter of 1 inch its mass would probably be more than 500 tons. If oxygen gas at atmosphere pressure could be magnified until the nuclei were each equal to the mass of the sun, we would have the sidereal universe reproduced in which the mean distance between atoms would approximate the mean distance between the fixed stars of the universe. Since the atomic weight of oxygen is 16 the atom is supposed to have eight electrons revolving around its nucleus. If we apply the same analogy of magnification to the structure of the oxygen atom we would have a system of eight satellites in which the relative distances between the revolving electrons and the central nucleus would approximate the distances of the eight planets from the sun. Thus, in oxygen gas the sidereal universe, with its stars and revolving planets, is reproduced in miniature.

It will be seen that the structure of gases counterfeits on a very small scale the structure of the great sidereal universe. Since all the forces acting in the nuclear atom are electrical, may not the forces acting in the stellar universe be electrical? Is not the force of universal gravitation electrical? Should not the universality of law lead us to infer that the force of gravitation is an electromagnetic force?

It will be seen from the preceding description that the form of the atom is that of a flat disk, which probably possesses elasticity. It was formerly supposed that atoms were spheres of infinite hardness, and, of course, without elasticity. The atom, and in fact all matter, is immersed in a medium called ether, which is continuous, frictionless, and pervades all space. Ether is the universal carrier of the energy of light, heat, electricity, and X-rays. Hydrogen has been called the smallest and lightest of the elements, but the sun, stars, and nebulae yield still smaller atoms called proto-hydrogen, asterium, and nebulium. The atoms of these very primitive forms of matter are simpler in their arrangement, and easier to calculate than most terrestrial elements. Working in the dark the alchemist of the Middle Ages attempted the transmutation of metals, without even knowing the nature of his problem. Science has now unveiled the secret of transmutation, by observing Nature's process of changing the heaviest element into a series of different products. The alchemist vainly sought to change mercury into gold. We now know that mercury might be changed into gold if we could expel from its atoms one α -particle and a β -particle; or if the metal thallium could be made to expel an α -particle it would become like atoms of gold. This has not yet been done, but it is possible that it might be done by the application of an electric current of some million volts.

The principal weight of the atom lies in its nucleus, but the nucleus is very small compared with the size of the atom. It contains so-called "sub-atoms" and electrons in association with positive electricity. The electric charge of the nucleus is therefore overwhelmingly positive. In the breaking up of atoms by radio-activity, the α -particles (helium atoms) and the β -particles (electrons) are thrown off from the nucleus. In the outer region of the atom there is a sufficient number of negative electrons to balance the central positive charge. It is this outer region that controls the chemical and much of the physical influence of the atom. It will thus be seen that the radioactive charge is connected with the nucleus, while chemical and electro-chemical properties are controlled by the outer rings of electrons. It is now known that there are relatively few electrons revolving around the nucleus, probably not more than half of the number representing its atomic weight, in which hydrogen is the unit.

The period of revolution around the nucleus by the electrons appears to be identical with Kepler's harmonic law of planetary motion, in which electrical force, varying inversely as the square of the distance, takes the place of

the force of gravitation. The lightest atom is supposed to have but one revolving electron. This limits the smallness of the atom, because you could not have an atom with no revolving electron. The smallest atom resembles the earth with its one satellite. The heavy atoms have far greater numbers; an atom of mercury would possess a hundred electrons, which is ten times as many satellites as Saturn has.

Lockyer has shown that the younger and hotter stars contain elements fewer in number and simpler in structure than the older and cooler stars. In this fact we face the gigantic evolution of matter from the primitive source of the universal ether to the complexity of terrestrial organic matter. The mighty machinery of the cosmos is immortal in its operation. Ceaseless change is the only constant thing in Nature. The complete cycle of change leads matter through all its phases from the simplicity of the hottest star to the complexity of matter in the planets and in our cool earth.

A recent article by O. Lehmann, on the discovery of the formation of liquid crystals, incidentally confirms the theory that atoms are flat and not spherical. He assumes that the molecules of these crystals are tiny flat plates whose surfaces are perpendicular to the optical axis. He says, "The molecules easily glide over one another in a direction parallel to their flat surfaces," and concludes that the crystals are combinations of plate-like molecules. Since molecules are small groups of atoms and some molecules consist of single atoms, it follows that disk-shaped atoms would lend themselves to the formation of flat molecules.

It is probable that the atom is elastic; not perhaps by the pressure that could be secured artificially in the laboratory, but by the gigantic gravitational pressure of the interior of the planets and stars. The earth's interior is so hot that if its pressure were released it would explode into gases of very high temperature. The pressure of gravitation near the earth's centre amounts to millions of pounds to the square inch, and there matter is reduced to the density of platinum. Under this force liquids yield like a sponge. Owing to the enormous pressure that gravitation imposes on the earth it is compacted into a dense mass as rigid as that of a ball made from nickel steel armour plate.

We now appear to be on the verge of further discoveries in the nature of matter which may lead to a knowledge of the mysterious unknown ether. All intelligent people are interested in new information regarding the swift electrons that light our cities, propel our street cars, operate factories, transmit speech, carry wireless messages, and serve man in hundreds of ways. A host of eminent scientists have framed a science of radio-activity which has changed the entire theory of matter, involving conceptions that are difficult to explain to those who have not specialised in physical science. Even the accomplished physicist Sir William Crookes says that the conceptions of atomic physics are often hard to understand. We are, unfortunately, lacking in gifted interpreters of physical science, such as the nineteenth century furnished. Darwin, Huxley, Spencer, and Tyndall could clearly explain to the uninitiated, in simple words, the most intricate scientific discoveries of their period.

A SIMPLE METHOD FOR VAPOUR-DENSITY DETERMINATIONS.

(PART XIII.).

By PHILIP BLACKMAN.

(Continued from p. 110).

As has already been pointed out in the *Journal of Physical Chemistry*, 1908. xii., 676, the apparatus can most advantageously be used in determining, quickly and accurately, quantitatively the components of binary mixtures. Thus, if d_1 , d_2 be the vapour-densities (supposed known)

Mixture.	d_4^{20}	RESULTS. ($w_2 = 100 - w_1$).							Per cent w_1, w_2 found.	Actual weights. Grm.	Actual per cent.
		P. Mm.	L. Mm.	L _c . Mm.	l. Mm.	V. Cc.	w. Grm.	t ₁ . C.			
CH ₃ I	70.93	758	351	363	210	152.1	0.6720	16.5	47.8	0.3211	47.8
C ₂ H ₅ I	77.92								52.2	0.3509	52.2
CCl ₄	76.90								64.3	0.3474	64.3
C ₂ H ₅ Br	54.48	763	348	360	198	120.3	0.5403	17.0	35.7	0.1929	35.7
CH ₃ .OH	16.00								23.0	0.0302	23.0
C ₂ H ₅ .OH	23.00	749	355	367	256	180.4	0.1312	17.5	77.0	0.1010	77.0
(C ₂ H ₅) ₂ O	37.00								87.0	0.2408	86.9
(CH ₃) ₂ OC	29.00	749	350	362	240	189.7	0.2772	16.5	14.0	0.0364	13.1
CH ₃ .CO ₂ .C ₂ H ₅	44.00								91.6	0.2106	91.7
CH ₃ .CN	20.52	760	340	351	223	184.3	0.2300	18.0	8.4	0.0194	8.3
C ₆ H ₆	39.00								83.8	0.3350	83.7
CHCl ₃	59.67	761	341	353	201	179.1	0.4000	19.0	16.2	0.0650	16.3
C ₅ H ₅ N	39.50								85.3	0.3422	85.3
C ₅ H ₁₁ .OH	44.00	760	335	349	210	188.2	0.4010	19.5	14.7	0.0588	14.7
C ₅ H ₅ .OH	29.00								52.2	0.2506	52.1
(CH ₃ .CO) ₂ O	51.00	766	338	351	187	185.3	0.4811	20.0	47.8	0.2305	47.9
CH ₃ .COCl	39.22								59.6	0.2455	59.9
CH ₃ .COH	22.00	761	320	331	174	180.1	0.4098	19.5	40.4	0.1643	40.1
C ₂ H ₄ Cl ₂	49.45								52.0	0.1857	52.0
CH ₃ .CO ₂ H	30.00	757	325	337	208	189.3	0.3570	18.5	48.0	0.1713	48.0
CH ₃ I	70.93	758	315	327	235	184.7	0.3784	19.5	70.5	0.2668	70.5
C ₂ H ₅ Br	54.48								29.5	0.1116	29.5
CH ₃ .OH	16.00								72.9	0.1520	73.0
(CH ₃) ₂ CO	29.00	761	312	322	201	180.3	0.2081	18.5	27.1	0.0561	27.0
CH ₃ .OH	16.00								6.4	0.0108	6.4
(C ₂ H ₅) ₂ O	37.00	763	311	322	198	178.0	0.3090	19.0	93.6	0.2892	93.6
C ₂ H ₅ .OH	23.00								63.6	0.2534	63.5
(C ₂ H ₅) ₂ O	37.00	760	309	316	184	174.7	0.4008	17.5	36.4	0.1464	36.5
(CH ₃) ₂ CO	29.00								33.0	0.0857	33.0
C ₂ H ₅ .OH	23.00	757	300	310	184	188.3	0.2597	16.0	67.0	0.1740	67.0
CH ₃ .CN	20.52								49.1	0.1345	50.0
C ₆ H ₆	39.00	755	301	309	187	186.2	0.2690	16.0	50.9	0.1345	50.0
CH ₃ .CO ₂ .C ₂ H ₅	44.00								71.4	0.3675	71.0
C ₆ H ₆	39.00	759	299	310	171	184.3	0.5175	16.5	28.6	0.1500	29.0
C ₅ H ₅ N	39.50								63.9	0.1345	64.0
C ₅ H ₅ .OH	29.00	764	197	209	147	181.5	0.2101	18.0	36.1	0.0756	36.0
C ₅ H ₁₁ .OH	44.00								62.4	0.1770	61.6
C ₅ H ₅ .OH	29.00	763	199	211	136	178.1	0.2890	17.0	37.6	0.1110	38.4
(CH ₃ .CO) ₂ O	51.00								16.3	0.0650	16.0
C ₅ H ₁₁ .OH	44.00	759	196	205	129	191.6	0.4060	19.0	83.7	0.3410	84.0
CH ₃ .CO ₂ H	30.00								26.9	0.0861	26.9
CH ₃ .COH	22.00	757	181	190	100	189.4	0.3191	20.0	73.1	0.2330	73.1
C ₂ H ₄ Cl ₂	49.45								73.4	0.2364	73.8
CH ₃ .COH	22.00	761	181	192	121	186.2	0.3202	19.5	26.6	0.0838	26.2
CH ₃ .CO ₂ H	30.00								45.8	0.2303	45.0
C ₆ H ₅ .NO ₂	61.52	750	178	188	102	184.1	0.5117	15.0	54.2	0.2814	55.0
C ₆ H ₅ .NH ₂	46.52								53.7	0.2656	53.1
C ₆ H ₅ .NO ₂	61.52	757	175	186	112	181.8	0.4998	16.0	46.3	0.2342	46.9
CHCl ₂ .CO ₂ H	64.45								47.9	0.2406	48.0
CH ₃ .CO ₂ H	30.00	765	177	187	100	178.4	0.5011	18.5	52.1	0.2605	52.0
C ₆ H ₅ .NH ₂ .CH ₃	53.52								80.4	0.3824	80.0
C ₆ H ₅ .N(CH ₃) ₂	60.52	760	163	177	111	189.3	0.4780	17.5	19.6	0.0956	20.0
[1:2].CH ₃ .C ₆ H ₄ .NH ₂	53.52								61.1	0.2994	61.0
(C ₆ H ₅) ₂ NH	84.52	758	164	178	115	186.4	0.4908	19.0	38.9	0.1914	39.0
C ₆ H ₅ .COCl	70.22								47.8	0.2136	48.0
CH ₃ .COCl	39.22	761	160	170	105	183.2	0.4451	19.0	52.2	0.2315	52.0
C ₆ H ₅ .CH ₂ Cl	63.22								18.9	0.0927	18.6
C ₂ H ₄ Cl ₂	49.45	766	161	172	102	180.0	0.5010	19.0	81.1	0.4083	81.4
[1:4].CH ₃ .C ₆ H ₄ .NO ₂	68.52								19.5	0.0989	20.0
[1:4].CH ₃ .C ₆ H ₄ .NH ₂	53.52	760	150	160	98	177.7	0.4944	18.5	80.5	0.3955	80.0
CCl ₄	76.90								97.0	0.6352	97.0
[1:4].C ₆ H ₄ Cl.NH ₂	63.74	763	152	164	101	175.0	0.6548	17.0	3.0	0.0106	3.0
C ₆ H ₅ .COH	53.00								86.5	0.4309	86.1
CH ₃ .COH	22.00	749	150	160	87	171.4	0.5009	17.5	13.5	0.0700	13.9
C ₆ H ₆	39.03								57.2	0.2087	57.0
C ₆ H ₅ .CH ₃	46.04	761	333	348	220	188.4	0.3661	20.0	42.8	0.1574	43.0
C ₆ H ₆	39.03								35.3	0.1441	35.1
[1:3:5].C ₆ H ₃ (CH ₃) ₃	60.06	765	330	340	221	185.9	0.4116	19.5	64.7	0.2675	64.9
C ₆ H ₆	39.03								47.1	0.1923	47.1
C ₆ H ₅ .Cl	56.22	760	325	339	212	182.0	0.4091	18.0	52.9	0.2168	52.9
C ₆ H ₅ .CH ₃	46.04								27.2	0.1316	27.0
[1:3:5].C ₆ H ₃ (CH ₃) ₃	60.06	766	310	322	201	179.8	0.4872	19.5	72.8	0.3556	73.0
C ₆ H ₅ .CH ₃	46.04								6.8	0.0335	7.0
C ₆ H ₅ .Cl	56.22	760	312	322	200	176.3	0.4789	20.0	93.2	0.4454	93.0
[1:3:5].C ₆ H ₃ (CH ₃) ₃	60.06								38.8	0.1720	39.0
C ₆ H ₅ .Cl	56.22	763	300	310	200	171.5	0.4411	20.0	61.2	0.2691	61.0

of the constituents of a mixture, then their relative percentage weights, w_1 and $100 - w_1$, respectively, are obtained from the equation—

$$d_2 w_1 + d_1 (100 - w_1) = \frac{100 d_1 d_2 \rho LV (L_c - l)}{31068 w_1 L_c (273 + t_1)}$$

(It will be observed that, if $d_1 = d_2$, this equation gives no solution for w_1 or $100 - w_1$; that is, if the two constituents have exactly equal vapour densities the determination of the vapour-density of the mixture gives no indication as to the relative proportions of the constituents).

ERRATA.—P. 75, col. 1, and p. 110, in the heading to Table, for "Min." read Min."

(To be continued).

POLYPEPTIDE-HYDANTOINS.

By TREAT B. JOHNSON, Sheffield Scientific School, Yale University.

CARBON dioxide is one of the products of decomposition when certain proteins undergo hydrolysis, under normal conditions, by digestion with aqueous solutions of acids and alkalis. Mörner observed the formation of this acid anhydride during an investigation of the action of hydrochloric acid (sp. gr. 1.124) on horn at 92°, but no quantitative determination of the gas was made, and no special significance attributed by him to its formation (*Zeit. Phys. Chem.*, 1901, xxxiv., 207). Lippich confirmed this observation several years later, and showed that this anhydride is a normal product of hydrolysis of other proteins (*Zeit. Phys. Chem.*, 1914, xc., 441). He also made the important observation that the quantity actually formed is dependent on the nature of the hydrolytic agent employed. Quantitative determinations of the amount of the gas evolved from several proteins under specific conditions revealed the interesting fact that the maximum quantity is obtained when an alkali, as potassium or barium hydroxide, is used as the hydrolytic agent. In no case did Lippich fail to detect the presence of this substance among his products of hydrolysis. The actual percentages obtained by hydrolysis of five different proteins with potassium hydroxide solution are recorded in Table I.

For his acid hydrolyses Lippich used 33 per cent sulphuric acid. When these same proteins were broken down by heating with this reagent entirely different analytical results were obtained. The combinations in the proteins productive of carbon dioxide were more resistant to hydrolytic changes, under these conditions, and the maximum amount of this gas was not obtained until after twenty-five to twenty-seven hours digestion. The percentages found are recorded in Table I.

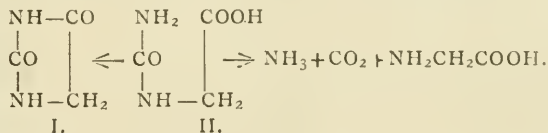
TABLE I.

Protein.	Carbon dioxide.	
	By acid hydrolysis.	By alkali hydrolysis.
	Per cent.	Per cent.
Parahämoglobin ..	$\left\{ \begin{array}{l} 0.352 \\ 0.332 \\ 0.370 \end{array} \right\}$	2.09
Egg albumin.. ..	0.336	2.77
Serum globulin ..	0.364	$\left\{ \begin{array}{l} 2.41 \\ 2.38 \end{array} \right\}$
Elastin	0.130	0.680
Keratin	0.372	$\left\{ \begin{array}{l} 4.63 \\ 4.53 \end{array} \right\}$

In the course of investigations now in progress in this laboratory, dealing with the study of new hydantoin and thiohydantoin combinations of biochemical interest, I had occasion to determine whether gaseous products are evolved by hydrolysis of pure fibroin, and also casein. I now find that both these proteins break down on hydrolysis with sulphuric acid with evolution of carbon dioxide, and obtained from casein 0.35 per cent of its weight in the

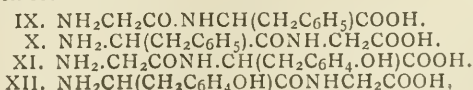
form of this gas, while three quantitative experiments with fibroin gave the values 0.20, 0.27, and 0.25 per cent respectively. When boiling, 30 per cent barium hydroxide solution was used for the hydrolysis of fibroin (the action of barium hydroxide on casein is being investigated), we obtained the values 1.08 and 1.05 per cent of carbon dioxide. In other words, in the cases of the two proteins elastin and fibroin, about five times as much carbon dioxide is produced by alkaline hydrolysis as is obtained by digestion with sulphuric acid. By inspection of Table I. it will be seen that the greatest increase was obtained by hydrolysis of keratin. The results obtained with fibroin have special significance because the production of carbon dioxide in this case does not result from the breaking down of cystin, as this protein is free from sulphur.

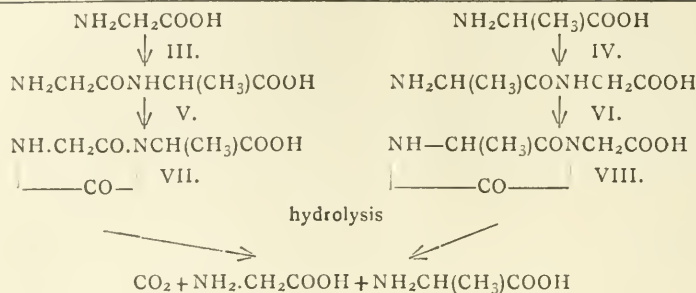
The marked difference in behaviour towards acids and alkalis and the further fact that the quantity of carbon dioxide formed by hydrolysis is not proportional to the amount of arginine present in the respective proteins, suggest that urea combinations are the precursors of this gaseous hydrolytic product. Carbon dioxide would be a normal product of hydrolysis of such groupings, and their destruction would be more easily accomplished by the action of alkalis than with acids. Lippich has advanced the idea that uramido acid, of which hydantoic acid II. is the prototype, are the types of urea combinations which functionate in these changes. Such groupings, as is well known, are hydrolysed by alkalis with formation of α -amino acids, carbon dioxide, and ammonia. On the other hand, when heated with acids, they easily undergo inner condensation with transformation into their corresponding anhydrides or hydantoina I. The latter compounds are very resistant to further hydrolysis with acids as has been shown by investigations in this laboratory.



While this explanation of Lippich's is in concordance with the chemical nature of hydantoic acids, on the other hand, these compounds (II.) do not represent the only types of uramido combinations which can undergo hydrolysis with formation of carbon dioxide and α -amino acids. One point needs to be taken into consideration here, and that is the fact that for every molecule of carbon dioxide formed by hydrolysis of a hydantoic acid II. an equivalent amount of ammonia must also be obtained. Apparently this ratio $\text{CO}_2:\text{NH}_3$ has never been established quantitatively in the case of a single protein.

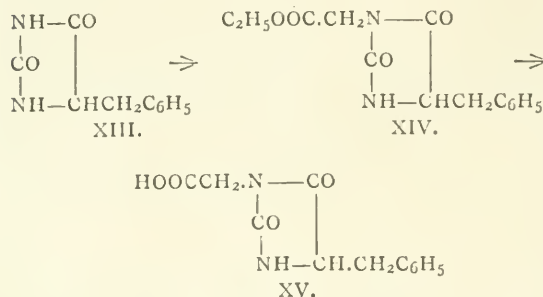
Theoretically it is possible to link together two α -amino acids in a cyclic urea combination in such a manner that the resulting compound will undergo hydrolysis with production only of carbon dioxide and α -amino acids. If we choose glycocoll III. and alanine IV. as the two amino acids and combine them in the form of hydantoina as represented by formulae VII. and VIII., two isomeric cyclic combinations will be obtained which will fulfil the above conditions. In other words, they are cyclic derivatives of the two isomeric dipeptides—glycylalanine V. and alanyl-glycine VI. respectively, in which the characteristic polypeptide groupings of the dipeptides have been preserved. Such combinations are the representatives of a new class of hydantoina, to which we have assigned the name *poly-peptide-hydantoina* (see accompanying scheme, next page). The hydantoin derivatives of the polypeptides—glycyl-phenylalanine IX., phenylalanylglycine X., glycyltyrosine XI., and tyrosineglycine XII.—are now being investigated. Their formulae are—



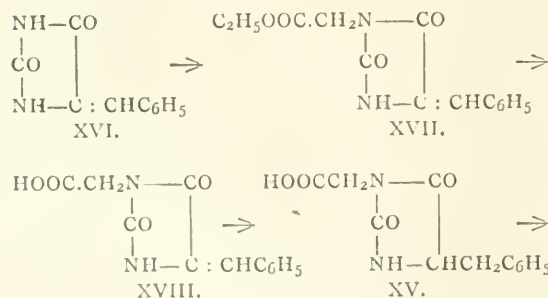


The polypeptide-hydantoin XV. (m. 184–185°) has already been synthesised, and two methods have been developed for its preparation which are apparently of general application.

1. Alkylation of 4-benzylhydantoin XIII. (Wheeler and Hoffman, *Am. Chem. Journ.*, 1911, xlv., 368) with ethyl chloracetate with formation of the ester XIV. (m. 157°), which is easily converted into the *polypeptide-hydantoin* XV. by saponification.



2. Alkylation of 4-benzalhydantoin XVI. (Ruhemann and Cunningham, *Journ. Chem. Soc.*, 1899, lxxv., 958; Ruhemann and Stapleton, *Journ. Chem. Soc.*, 1900, lxxvii., 246; Wheeler and Hoffman, *loc. cit.*), with ethyl chloracetate with formation of the ester XVII. (m. 174°). The latter gives by saponification the unsaturated acid XVIII. (m. 258°) which undergoes reduction smoothly giving the *polypeptide-hydantoin* XV.



Other methods for synthesising hydantoin compounds of this type (and their sulphur analogues) are being developed. This work will include not only the study of hydantoin derivatives of dipeptides but also tripeptide combinations of analogous constitution, and also an investigation of their behaviour towards hydrolytic agents and enzymes.—*Proceedings of the National Academy of Sciences, U.S.A.*, ii., No. 2.

EXPERIMENTS ON THE INFLUENCE OF COMPOSITION UPON THE CORROSION OF STEEL.*

By LESLIE AITCHISON, M.Met.

PART II.

The following results show the effect of ordinary tap-water upon the same steels whose corrosion in 3 per cent sodium chloride solution, in 1 per cent and 10 per cent sulphuric acid has been presented already. The results in water correspond more to the ordinary "rusting" which occurs so regularly in everyday experience. The method of preparation of the steels was exactly the same as in the previous experiments, and in this case the pieces were suspended in tap-water in glass beakers in the dark. They were immersed during 77 days, but in this case the water was renewed seven times (at regular intervals) during the progress of the corrosion, the rust adhering to the pieces being shaken off gently before the pieces were put into the fresh water. The pieces after corrosion were cleaned and dried in the usual manner. As before, the results given of loss of weight are the mean of concordant duplicate experiments, and in the tables the loss of weight in gms. per square cm. is multiplied by a hundred.

SERIES I.—Pure Iron and Carbon Steels.

(The complete analyses of all the steels used in all the experiments were given in Part I., *q.v.*.)

No. of steel.	C per cent.	Loss of weight for cm. 2 × 100.
1	0.07	0.875
2	0.19	0.860
3	0.39	0.866
4	0.50	0.88
6	0.68	0.89
10	0.89	0.92
8	1.05	0.92
9	1.25	1.02
7	1.46	1.01

The steels do not display the same regularity in their corrosion in tap-water that they did in the 3 per cent sodium chloride solution or in the 10 per cent sulphuric acid. So far as they may be compared with any of the results obtained previously, they appear to show a greater similarity to the effects produced in 1 per cent sulphuric acid than any other. There is, however, again the fall of corrosion at first with the rising carbon from bar iron to steel with 0.4 per cent of carbon noticed in the case of brine and the 10 per cent sulphuric acid. (This is referred to again in Part III., *prox.*). After this original fall there is a regular, gradual rise of the corrosion from 0.4 per cent to 1.46 per cent of carbon (*cf.* Fig. 1). Comparing with the corrosion in brine it may be seen that the actual loss of weight is almost as great in the tap-water as in the 3

* A Contribution to a General Discussion on "The Corrosion of Metals" before the Faraday Society, December 8, 1915.

per cent sodium chloride solution, the minimum ratio being 0.77 for the steel containing 0.89 per cent carbon, and the maximum being 0.89 in the 1.46 per cent carbon steel.

In Series II. there are several prominent irregularities, though many interesting results emerge. In the tungsten steels the addition of the third element has increased the corrosion throughout the series. (For the corresponding pure carbon series the loss in grms. per square cm. $\times 100$ is 0.9). The increase of corrosion over that experienced by the pure carbon steels is not so great in any part of the series as was the case with the attack by sodium chloride solution. The definite maximum at 15 per cent tungsten is quite unique to the water corrosion. The microstructure of this steel shows that it has very thin walls of a carbide overlying the solid solution (*cf.* Arnold and Read, *Found. Inst. Mech. Eng.*, 1914, 239). This is the first steel in the series which shows this carbide quite free (It may be seen from Arnold and Read's paper that the "saturation" point of the tungsten series occurs at about 11.5 per cent tungsten and 0.72 per cent carbon, and that consequently any excess of tungsten over this may possibly appear as structurally free carbide). It might be expected in consequence of this change of microstructure that some difference in the corrosion would be introduced by the new constituent. (This point, and possible conditions of

corrosion by water—the steel with the highest proportion of chromium does not corrode at all, whilst the one that was unattacked by the sodium chloride solution is now corroded to a slight extent. With increasing chromium the corrosion falls throughout the series, the steel containing the largest proportion of free carbide being the least attacked. In this corrosion medium there is no increased attack with the lower percentages of chromium over that sustained by the corresponding pure carbon steel, as was the case in the brine.

The addition of the vanadium has produced a relatively small variation in the corrodibility of the steel, though curiously enough it has made the corrosion by water less than for the pure carbon steels, whilst in the case of the sodium chloride solution the presence of the vanadium caused an increased loss. In the sodium chloride solution and in 1 per cent sulphuric acid there was noticed a general tendency to a decrease of corrosion with an increase of vanadium. This is supported by the action—in this case—by the water.

In Series III., in the tungsten set there is shown the interesting fact that the addition of 3 per cent of tungsten has produced a decrease of the corrosion. This was noticed also in the attack by both 1 and 10 per cent sulphuric acid, but was not found in the case of the sodium chloride solution—where an increased corrosion was

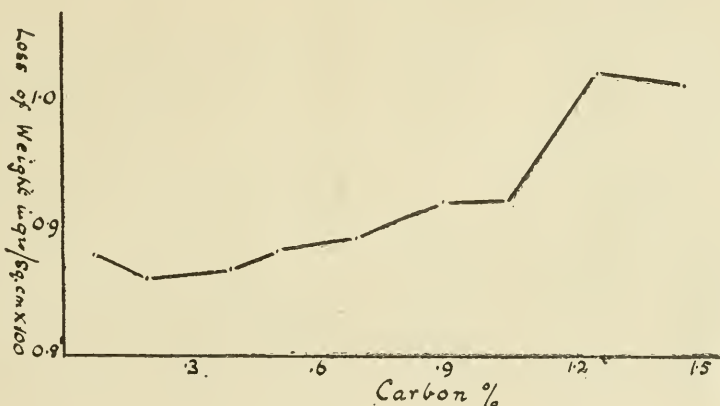


FIG. 1.

difference between the action in water and in sodium chloride solution or sulphuric acid, are discussed in Part III., *prox.*). Although the proportion of this excess carbide rises higher in the next steel (the one containing 21.5 per cent), the form of it changes to a considerable extent. From being of the nature of cell walls it becomes more granular, and does not surround the crystals to the same extent.

The cobalt steels give results differing very much from those obtained previously. In place of the very regular fall of corrodibility throughout the series, noticed with these other media, the attack by water is distinctly irregular. Still more peculiar is the maximum attack with the steel containing the largest percentage of cobalt. This following upon the minimum of corrosion with the next highest steel in the series is difficult of explanation. With the exception of this latter steel it will be noticed that the addition of the cobalt has caused an increase in the corrosion over that of the pure carbon steel, though once again not to the same extent as in the attack by the brine.

The chromium series presents one feature of particular interest. In the corrosion by sodium chloride solution, and 1 per cent sulphuric acid, the steel containing 19.46 per cent of chromium was quite or almost unattacked by the medium, whilst the one with 23.7 per cent chromium was attacked rather more. In this case—the

experienced. In this series with water there is quite a regular fall to a minimum followed by a rise, to be noticed.

The vanadium steels, though irregular, may be taken to show that the addition of this small percentage of vanadium has had practically no effect upon the corrodibility. This is not at all the result obtained with the other three corrosion media in which a distinct increase of the corrosion was obtained as a whole. The 2 per cent chromium steels in this case—unlike the results obtained with sodium chloride and sulphuric acid—show a slight though firm decrease at all three percentages of carbon.

The nickel steels give apparently regular results and show themselves largely in conformity with the attack by sodium chloride and by the 10 per cent sulphuric acid. In these three cases—water, brine, and 10 per cent acid—there is a distinct rise of corrosion with increase of carbon at the start, followed by a fall to the material with the highest proportion of carbon. At the two ends of the series (in water) the corrodibility has been decreased by the presence of 3 per cent of nickel, whilst in the middle (from 0.3 to 0.8 per cent carbon) it has been increased. The manganese steels are quite irregular in their behaviour, though it appears fairly certain that the addition of manganese causes an increased corrodibility in water, as well as in the other media.

SERIES II.

Tungsten Steels.

No. of steel.	C per cent.	W per cent.	Loss of weight per cm. ² × 100.
48	0.74	2.36	0.970
46	0.72	5.37	0.930
45	0.70	9.74	0.976
47	0.74	14.96	1.100
44	0.73	21.5	0.940
43	0.68	26.3	0.970

Cobalt Steels.

No. of steel.	C per cent.	Co per cent.	Loss of weight per cm. ² × 100.
63	0.73	2.68	0.94
64	0.65	5.50	0.95
67	0.75	11.18	1.06
65	0.75	16.95	0.74
66	0.72	20.85	1.12

Chromium Steels.

No. of steel.	C per cent.	Cr per cent.	Loss of weight per cm. ² × 100.
23	0.84	0.99	0.845
25	0.84	4.97	0.652
24	0.85	10.15	0.452
26	0.88	15.02	0.453
27	0.85	19.46	0.154
28	0.85	23.70	0.000

Vanadium Steels.

No. of steel.	C per cent.	V per cent.	Loss of weight per cm. ² × 100.
33	0.60	0.71	0.90
34	0.63	2.32	0.85
35	0.93	5.81	0.86
36	1.07	10.3	0.70
37	1.10	12.15	0.85

SERIES III.

Tungsten Steels.

No. of steel.	C per cent.	W per cent.	Loss of weight per cm. ² × 100.
50	0.20	3.09	0.793
49	0.47	3.22	0.759
51	0.58	3.16	0.642
52	0.88	3.07	0.742
53	1.08	3.11	0.800

Vanadium Steels.

No. of steel.	C per cent.	V per cent.	Loss of weight per cm. ² × 100.
38	0.11	0.17	0.900
39	0.38	0.22	0.820
40	0.73	0.21	0.995
41	0.96	0.22	0.932
42	1.3	0.21	1.035

Chromium Steels.

No. of steel.	C per cent.	Cr per cent.	Loss of weight per cm. ² × 100.
29	0.33	1.97	0.800
30	0.52	2.01	0.825
31	0.64	2.05	0.812

Nickel Steels.

No. of steel.	C per cent.	Ni per cent.	Loss of weight per cm. ² × 100.
54	0.07	3.07	0.802
55	0.28	3.13	0.870
56	0.48	2.94	1.086
58	0.76	3.08	0.966
57	0.88	2.97	0.895

Manganese Steels.

No. of steel.	C per cent.	Mn per cent.	Loss of weight per cm. ² × 100.
19	0.28	0.94	0.900
20	0.48	0.91	0.960
11	0.76	0.83	0.872
22	0.87	1.01	1.43

SERIES IV.—Copper Steels.

No. of steel.	C per cent.	Cu per cent.	Loss of weight per cm. ² × 100.
59	1.18	0.48	1.03
60	0.59	1.06	0.820
61	0.38	2.52	0.980
62	0.30	4.78	1.10

The results obtained with the copper steels are faintly reminiscent of the attack by 10 per cent sulphuric acid. In general, too, there is an increased corrosion over that sustained by the pure carbon steels, as was the result with sodium chloride solution.

The tap-water employed in the foregoing experiments gave the following mean analysis:—

	Grains per gallon
Total solids..	7.30
SiO ₂ ..	0.56
Fe ₂ O ₃ and Al ₂ O ₃ ..	0.21
CaCO ₃ ..	1.04
Chlorine ..	0.89
H ₂ SO ₄ ..	1.70
MgO ..	0.51
Alkaline salts: H ₂ O in combination, &c.	2.39

Oxygen consumed, 2.4 parts per million of water.

(To be continued).

INTERNATIONAL CROP REPORT AND
AGRICULTURAL STATISTICS.

THE February issue of the *Statistics*, published by the International Institute of Agriculture, shows in a table the data from cereal harvests in progress or finished in Argentina and Australia, the data confirming the good forecasts reported in the previous issues. These are followed by reports on areas seeded with autumn cereals for 1915-16, and on the condition of these crops in Northern Hemisphere countries.

Among new data on areas seeded are the following:—

France.—Wheat, 5,034,510 hectares, or 91.4 per cent of the corresponding area in 1914-15; rye, 920,975, or 88.6 per cent; barley, 99,730, or 66.6 per cent; and oats, 684,980, or 88.4 per cent.

Spain.—Wheat, 3,984,879 hectares, or 106 per cent; rye, 608,159, or 95 per cent; barley, 1,706,220, or 121 per cent; and oats, 433,188, or 117 per cent.

Canada.—Winter wheat, 445,472 hectares, or 85.1 per cent of the corresponding area in 1914-15.

Crop conditions are reported from several countries:—Slight backwardness in growth in France and Great Britain, where, however, favourable weather in January greatly benefited the crops. In Italy, Switzerland, India, Algeria, and Egypt crops are in satisfactory condition.

Following on the above material are tables with 1915 harvest data in Northern Hemisphere countries, where, however, no important change has occurred in the data given in January.

The Agricultural Part of the *Statistics* ends with data from recent returns of live stock in France in December, 1915, and in the United States at January 1 last. In the latter country there appears a notable increase in the number of cattle, viz., 61,441,000 head at January 1, 1916, compared with 58,329,000 at January 1, 1915, being an increase of 3,112,000 head, or 5.3 per cent.

The Commercial Part contains tables of imports and exports, stocks and prices of cereals and cotton on the principal markets as completely as possible under present circumstances.—*Bulletin of Agricultural and Commercial Statistics*, VIIth Year, No. 2. Rome, Feb., 1916.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 2, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Antiseptic Action of Substances of the Chloramine Group." By J. B. COHEN, F.R.S., H. D. DAKIN, M. DAUFRESNE, and J. KENYON.

The probability that the formation from proteins of substances containing halogen was an intermediate agent in the germicidal action of hypochlorites made it desirable to investigate systematically a number of substances containing the (NCl) group. Among the substances investigated, the most promising were the group of sulphochloramides first prepared by Chattaway. The following are the main results of this investigation:—

1. Almost all the substances examined containing the (NCl) group possessed very strong germicidal action.

2. The presence in the molecule of more than one (NCl) group does not confer any marked increase in germicidal power.

3. The germicidal action of many of these chloramine compounds is molecule for molecule greater than that of sodium hypochlorite.

4. Substitution in the nucleus of aromatic chloramines by Cl, Br, I, CH₃, C₂H₅, or NO₂ groups does not lead to any very great increase in germicidal activity. More commonly there is a moderate diminution.

5. The chloramine derivatives of naphthalene and other dicyclic compounds of sulphochloramide type closely resemble simpler aromatic chloramines in germicidal action.

6. The few bromamines examined show a slightly lower germicidal action than the corresponding chloramines, but sodium sulphobromamides are much more active than sodium hypobromite.

7. Derivatives of proteins prepared by the action of sodium hypochlorite and containing (NCl) groups are strongly germicidal. Blood serum inhibits their germicidal action to much the same extent as it does with sodium hypochlorite or the aromatic chloramines.

Among the above products *p*-toluene sodium sulphochloramide was selected as being on the whole most suitable for practical use. It is easily and cheaply made; it is relatively non-irritating to wounds; it is non-toxic and very soluble in water, and may be kept unchanged both in the solid state and in solution for a long period.

A table is appended giving bacteriological results obtained from about fifty compounds of this class.

"Structure of the Dicyonodont Skull." By I. J. B. SOLLAS and Prof. W. J. SOLLAS, F.R.S.

This is an account of a skull of *Oudenodon* studied in serial transverse sections. It supplements and confirms the authors' previous description of the skull of a *Dicyonodon* (*Phil. Trans.*, B, 1913, cciv.).

"Analysis of Agricultural Yield. Part III. The Influence of Natural Environmental Factors upon the Yield of Egyptian Cotton." By W. L. BALLS.

A discussion of all existing data for the behaviour of the Egyptian cotton crop under the conditions of field cultivation during five years as analysed by the author's method of plant-development curves.

The term pre-determination is given to the fact that a fluctuation may be due to causes acting at some date long prior to its visible appearance. Thus daily fluctuations in rate of flowering are due to environmental conditions existing a month beforehand. Many other reactions of crop to environment are inexplicable unless allowance is made for pre-determination.

It is shown that there is no factor of "season" as such. The action of such factors as weather and climate, soil-water and soil-fertility, are differentiated and traced in the various curves. The pre-dominant influence of an autumnal rise of water-table in determining yield of crop is indicated, and the sensitivity of the plant to root-asphyxiation is shown.

A discussion of the function of the root-system, and of the importance of the factors operating through it, is made possible by the nature of the data. The factor of varietal constitution is shown to be of relatively insignificant importance, as compared with environmental factors, in determining yield of crop.

The results of these three analyses show that yield of crop can be studied physiologically as yield of an average plant by statistical records of development, and these can be satisfactorily interpreted in terms of the limiting factors of environment, reacting upon inherited genetic properties of plant, provided that the phenomenon of pre-determination is taken into account.

"Function of Chlorophyll, Carotin, and Xanthophyll." By A. J. EWART.

In the assimilation of carbon dioxide chlorophyll acts as a light energising enzyme. It takes direct part in the cycle of chemical changes which have xanthophyll as an intermediate product, and glucose, levulose, formaldehyde, and oxygen as end-products. Most of the sugar is formed directly and not through the medium of formaldehyde.

A large part of the energy represented by this sugar is absorbed during the reconstruction of the chlorophyll molecule.

Apart from its protective function, carotin seems to be especially important as providing, during its photo-oxidation, the massive hydrocarbon combination in the phytol radicle of chlorophyll whose addition is necessary to convert the dicarboxylic glaucophyllin into the tricarboxylic chlorophyll. Carotin and xanthophyll are mutually transformable by the aid of metallic oxidases and reductases respectively. Oxidation in darkness is not necessarily the same as that taking place in light. An emulsion of carotin in light in the presence of copper sulphate and salt develops reducing sugar and formaldehyde, whereas in darkness, although slowly oxidised, no sugar or formaldehyde is produced.

The oxidation of chlorophyll, carotin, and xanthophyll is more rapid at high temperatures than at low ones.

SOCIETY OF CHEMICAL INDUSTRY (LONDON SECTION).

Ordinary Meeting, March 6, 1916.

Mr. ARTHUR R. LING in the Chair.

The following paper was read:—

"Analysis of Commercial Benzoles." By PERCY E. SPIELMANN and EDWARD G. WHEELER.

Well washed commercial benzoles containing up to 20 per cent of toluene are subjected to a simple distillation and extraction, and the determination of two specific gravities, whereby the percentages of benzene, toluene, carbon disulphide, and paraffin are obtained. The distillate up to 90° C. of 100 cc. of the benzole is made proportional to the quantity of toluene present. This figure is not appreciably disturbed by the presence of other constituents in the quantities that they usually occur. The difference between the specific gravity of the original liquid and that after the removal of carbon disulphide is proportional to the amount of the latter substance in the sample. The percentage of toluene being known, the specific gravity of the corresponding benzene-toluene mixture is known, and the difference between this specific gravity and that after removal

of the carbon disulphide is proportional to the amount of paraffin present. The benzene is found by difference. The actual figures obtained are evaluated by reference to one or two graphs. The accuracy of the method is:—Toluene, 1 per cent; paraffin, 0.5 per cent; carbon disulphide, 0.1 per cent. The quantity of impurities present in well washed benzoles are too small to have any appreciable effect on the results, except thiophene, which may cause 0.5 per cent error in the paraffin figure. The second half of the paper is occupied by tracing the mathematical evolution from one graph to the other.

Dr. H. G. COLMAN said that he had tried the method, and could confirm the authors' claims in regard to it.

A discussion was opened by Prof. W. A. BONE, F.R.S., on "*The Economy of Fuel*."

Prof. Bone said that the national aspects of fuel economy may be considered from two somewhat different standpoints, namely:—(1) In view of the economic situation created by the war, and the necessity of enforcing a policy of national economy in the utilisation of essential commodities as the best means of paying a colossal war debt, and (2) in view of the interests of that remoter, but nevertheless not far distant future, when our coal supply will be restricted by approaching exhaustion.

He thought that it could hardly be questioned that the chief material basis of the great industrial and commercial expansion of this country during the past century has been our abundant supplies of easily obtainable coal, which, until quite recent years, have given us a position of great advantage over all other countries.

It is also equally true that we can no longer claim any advantage in this respect over our two nearest competitors, and that our whole economic future is dependent on our ability to maintain abundant supplies of relatively cheap fuel, which in turn is limited by the probable duration, not of our total available supplies (which after all is only an academic question), but of our easily workable coal-seams in relation to present and future demands.

He then proceeded to analyse the figures for the world's coal resources issued by the International Geological Congress, 1913, from which it would appear that the world's total probable and possible reserves of coal of all kinds within 6000 feet of the surface amounts to 7,397,553 million metric tons, or approximately 6000 times the present total annual consumption. Of these reserves, 51 per cent are located in the United States, 16.4 per cent in Canada, 13.5 per cent in China, 5.7 per cent in Germany, and only 2.6 per cent in Great Britain.

The relative insignificance of the British coal reserves is a matter of which our commercial and ruling class seem to be profoundly ignorant, otherwise effective measures would have been taken long ago to check the criminal wastefulness of all classes of the community in using coal, and he suggested that scientific and technical societies should insist upon the Government taking immediate effective action, both in the direction of establishing some systematic supervision through a Fuel Control Board of fuel consumption in all large industrial areas, and of promoting scientific investigations on a large scale upon the better utilisation of coal.

He next pointed out that the Board of Trade returns for British outputs of coal do not include a vast amount which is left behind in the pits because, under our present individualistic system, colliery companies can make bigger profits by working the better classes of coal only. This pit wastage represented on the average about 25 per cent of the whole coal actually won in the mines, and the question of checking it was one of supreme importance.

The inferior grades of coal now left behind in the pits ought to be brought up and transformed at the pit-head into useful forms of energy for public purposes.

Dealing with the question of our exports of coal, which now amounted to about 100 million tons per annum, or about one-third of the total coal brought to the surface, he suggested the reimposition of the duty of 1s. a ton on

all exported coal, and an ear-marking of a portion of the revenue so accruing for investigations upon the problem of fuel economy.

With regard to the possible margins of realisable economies in the use of coal, he estimated that they would amount to at least 30 per cent of the total home consumption of coal, which now amounted to nearly 200 million tons per annum. The question was being dealt with by a strong Committee of Chemists, Engineers, and Technologists, recently appointed by the British Association, of which he was the Chairman, and he earnestly appealed to members of the Society, and to all who were interested in the use of coal for industrial purposes, to support and assist this Committee in its investigation.

A lengthy discussion ensued, in which Dr. C. CARPENTER, President of the Society, Prof. H. E. ARMSTRONG, Mr. WALTER F. REID, Mr. W. J. A. BUTTERFIELD, and others took part.

Messrs. Hopkin and Williams sent an exhibit of fine chemicals.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. F. H. GLEW, Mr. JAMES KEITH, Hon. Mrs. R. C. PARSONS, and Mrs. SYMONDS were elected Members of the Royal Institution.

Leeds University.—We have received from the Secretary of the University a pamphlet giving the general regulations relating to the Scholarships and Fellowships which will be awarded in 1916. The latest date of entry for Entrance Scholarships, both those awarded by the University and by Public Bodies, is May 27, and full information is given about the annual value, conditions, and periods of tenures. Details are also included concerning the Senior Scholarships and Studentships which are offered annually.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.**—Biochemical Society, 5.30. (In the Botany Building, Imperial College of Science and Technology, South Kensington, London, S.W.). (Annual General Meeting). "Preparation and Properties of Plant Pectins," by S. B. SCHRYVER and Miss D. HAVES. "Diphasic Action of Salts on the Chocolate Gel," by S. B. SCHRYVER and Miss M. HEWITT. "Differences between Natural Chlorophyll and so-called Artificial Chlorophyll," by I. JORGENSEN. "Supposed Origin of Life in Solutions of Colloidal Silica," by S. G. PAINE. Demonstration of Dialysis with Different Colloidal Membranes, by W. BROWN. Demonstration of an Electric Growth Recorder, by V. H. BLACKMAN.
- TUESDAY, 21st.**—Royal Institution, 3. "Sea Power as a Factor in the Evolution of Modern Races," by Prof. ARTHUR KEITH.
- Institution of Petroleum Technologists, 8. President's Address. "The Natural Gas Industry, its Progress and Importance," by J. A. LEO HENDERSON.
- WEDNESDAY, 22nd.**—Royal Society of Arts, 4.30. "The England of Shakespeare," by Rev. P. H. DITCHFIELD.
- THURSDAY, 23rd.**—Royal Institution, 3. "Organic Chemistry in War—Organic Products used as Propulsive and Explosive Agents," by Prof. H. E. ARMSTRONG.
- FRIDAY, 24th.**—Royal Institution, 5.30. "The Mechanism of Chemical Change in Living Organisms," by Prof. W. M. BAYLISS.
- Physical, 5. "New Method of Determining Ionic Velocities," by Mrs. GRIFFITHS. "Explanation of the Migration of Ions" and "Method of Exhibiting the Velocities of Iodine Ions in Solution," by S. W. J. SMITH.
- SATURDAY, 25th.**—Royal Institution, 3. "Radiations from Atoms and Electrons," by Sir J. J. THOMSON.

THE CHEMICAL NEWS.

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CRUM'S AND MARSHALL'S TESTS FOR MANGANESE.

By LEONARD DOBBIN, Ph.D.

I. Crum's Test.

IN 1845 Walter Crum (*Ann.*, 1845, lv., 219) described as a delicate test for manganese the familiar reaction in which lead peroxide is heated with dilute nitric acid, and the liquid to be tested for manganese is added to the mixture. When manganese is present the liquid exhibits, after the excess of lead peroxide has settled to the bottom, a purple-red colour, which Crum attributed to permanganic acid. The production of permanganic acid in a somewhat analogous manner was effected twenty-five years earlier by Forchhammer (*Thomson's Annals of Philosophy*, 1820, xvi., 133) in an investigation of manganic and permanganic acids, but no suggestion was made as to its formation being employed, or being capable of employment, as a test for manganese.

It is in Crum's paper that the earliest mention is made of the colour of dissolved permanganic acid, produced by aid of lead peroxide, being used as a means of recognising manganese; hence it would appear fitting that the reaction should be designated as Crum's reaction for manganese, and it is so designated by Wolcott Gibbs (*Am. Journ. Sci. and Arts*, 1852, [2], xiv., 205, 207), by Braun (*Zeit. Analyt. Chem.*, 1868, vii., 342), by Chatard (*Am. Journ. Sci. and Arts*, 1871, [3], i., 419), and by other noted chemists. This, however, is not the invariable usage, and it is rather surprising to find the reaction referred to as Volhard's reaction in Treadwell's "Qualitative Analysis (Hall's translation, 1903), and also to find it attributed to Hoppe-Seyler in papers by Leclerc (*Comptes Rendus*, 1872, lxxv., 1210), by Vogel (*Ber.*, 1875, viii., 1534), and also elsewhere. It seemed to be a matter of interest to inquire into any facts which might justify the suppression of Crum's name in connection with the reaction and the substitution for it of these other names. The results of the inquiry are noteworthy.

In an elaborate paper on the determination of manganese, Volhard discusses, amongst other things, the behaviour of manganous salts with lead peroxide, chlorine, bromine, &c., and the most important passage in the present connection is that in which he first alludes to the reaction here dealt with. This passage runs as follows (*Ann.*, 1879, cxcviii., 357):—"When only a small quantity of manganese is in solution and a considerable quantity of minium is dropped, all at the same time, into the hot nitric acid solution, more permanganic acid is produced than can form a precipitate with the remaining protoxide; the liquid then retains the colour of permanganic acid: that is the elegant manganese reaction of Walter Crum." There can thus be no doubt as to Volhard's opinion regarding the authorship of the reaction.

The present writer has not been able to ascertain who first referred to Volhard's reaction for manganese, but considers that a refinement of misrepresentation with respect to the authorship is attained in Merck's "Catalogue of Reagents," which ought to be a reliable compilation. It states (Merck's "Reagenzien-Verzeichniss," 3te Aufl., 1913):—

"Volhard's Reaction for Manganese.—When a substance containing manganese is heated with nitric acid and lead peroxide, a purple-red coloration of permanganic acid is produced.

"Crum's Reaction for Manganese. Is identical with Volhard's reaction."

As regards the association of the reaction with the name of Hoppe-Seyler, the facts are as remarkable and even more interesting. It would appear that Fresenius is responsible for this association.

Leclerc, when mentioning the use of this reaction for quantitative purposes in the paper previously referred to, adds a footnote stating that it had already been indicated by Hoppe-Seyler as a qualitative method of searching for manganese, and citing as authority the French translation of Fresenius's "Qualitative Analysis." Reference to two English editions of this book appears to justify Leclerc in thus citing Fresenius, since the latest English edition states (Fresenius, "Qualitative Analysis," 10th English edition, 1887, p. 122):

"If a few drops of a solution containing protoxide of manganese, and free from chlorine, are sprinkled on binocide of lead, nitric acid free from chlorine added, and the mixture boiled and allowed to settle, the solution acquires a red colour, from the formation of permanganic acid (Hoppe-Seyler)."

It is probable that most readers would conclude from the wording of this paragraph that Hoppe-Seyler is clearly indicated as the author of the reaction. This conclusion is not borne out, however, by a reference to the German original, since in order to convey in unambiguous terms the meaning of the author's words, giving due effect to his punctuation, the concluding portion of the paragraph should read:—"the solution acquires—from the formation of permanganic acid (Hoppe-Seyler)—a red colour" (Fresenius, "Qualitative Analyse," 1895, 16te Aufl., p. 166). Perhaps the English translators considered that the comma placed before the final clause of the paragraph sufficed to confine the connection of Hoppe-Seyler's name to that clause, but it seems likely that few would so interpret the reference. It is not improbable that the wording of the French translation to which Leclerc refers may be as liable to mislead on this point as that in the English version.

The particulars stated up to this stage would seem to indicate Fresenius as correctly representing the facts, and his translators (or at any rate his English translators) as obscuring his accuracy. This is not the whole matter, however. In the paper by Chatard previously referred to, the author states that "the delicacy of Crum's test for manganese is well known," and he endeavours to make the reaction the basis of a volumetric method. He does not mention Hoppe-Seyler, but nevertheless Fresenius, in his periodical report on advances in analytical chemistry, says with reference to this paper (*Zeit. Anal. Chem.*, 1872, xi., 308):—"For the determination of small quantities of manganese Chatard employs the reaction indicated by Hoppe-Seyler ('die von Hoppe-Seyler . . . angegebene Reaction') for the qualitative recognition of manganese, which depends upon the formation of permanganic acid. The latter occurs when manganese compounds are boiled with nitric acid and lead peroxide." Fresenius at this date (1872) must have had a deep-seated determination to connect the reaction with the name of Hoppe-Seyler since he suppresses Crum's name, which was given by the author, and introduces Hoppe-Seyler's instead. It is to be noted, however, that Fresenius does not expressly state that Hoppe-Seyler was the author of the reaction; he merely employs phraseology which—whether designedly or not—inevitably misleads readers into supposing that he was.

What, then, did Hoppe-Seyler do in connection with the reaction? In order to answer this question and to see the matter in its proper bearing it is necessary to go back to a paper by H. Rose (*Pogg.*, 1858, cv., 294), in which the author attributes the reaction to Walter Crum, and refers to its surprising delicacy, but asserts that the observed purple-red colour is not due to permanganic acid but to sesquioxide of manganese. Hoppe-Seyler controverts this assertion in a paper "On the Optical Distinguishing of Compounds of Sesquioxide of Manganese and of Permanganic Acid" (*Journ. Prakt. Chem.*, 1863, xc.,

303). He states:—"Solutions of the sesquisulphate, but pre-eminently of the sesquiphosphate, of manganese, especially when they are concentrated, exhibit such a fine purple colour that, so far as appearance is concerned, they might readily be mistaken for compounds of permanganic acid. H. Rose, who first described the preparation and behaviour of the beautiful sesquiphosphate, calls attention to this, and believes, further, that the purple-red colour of the liquid which is obtained according to Walter Crum by boiling peroxide of lead and nitric acid with a sample of a manganese compound must not be attributed, as this author assumed, to the formation of permanganic acid, but to that of sesquinitrate of manganese. . . ." "The optical behaviour of the liquid obtained according to W. Crum's method shows, however, in the most decisive manner that the colour is due to permanganic acid."

Hoppe-Seyler then shows that there are five bands in the absorption spectrum of dilute solutions of permanganates which are absent from similarly dilute solutions of sesqui-salts of manganese, and adds that "the liquid prepared according to W. Crum's process exhibits the five absorption bands of permanganic acid most distinctly." As in the case of Volhard, it is plain here also that Hoppe-Seyler had no doubts as to the real authorship of the reaction.

It is perhaps worth noting that Fresenius in his periodical report deals with Hoppe-Seyler's paper (*Zeit. Anal. Chem.*, 1864, iii., 137), but there correctly represents the author as mentioning Walter Crum's reaction, and explains parenthetically what this reaction is. It is, to say the least, remarkable that Fresenius should embody in his report a reference to "Walter Crum's reaction" in 1864, and that he should go out of his way to describe the same reaction in 1872 as "the reaction indicated by Hoppe-Seyler."

Merck's "Catalogue of Reagents" is at least consistent in its misrepresentation. It states:—

"Hoppe-Seyler's Reaction for Manganese.—Is identical with Volhard's reaction."

II. Marshall's Test.

In a short paper on "The Detection and Estimation of Minute Quantities of Manganese" (*CHEMICAL NEWS*, 1901, lxxviii., 76) Marshall points out that "the most delicate test for manganese in solution consists in converting it into permanganate, recognisable by the colour it imparts to the solution"; refers to Crum's method of effecting this conversion, and adds that "the test would be greatly improved by the use of an oxidising agent which is itself colourless and soluble." In an earlier paper (*Journ. Soc. Chem. Ind.*, 1897, xvi., 399) he had stated that persulphates cause the precipitation of peroxides when added to solutions of certain metallic salts, and that in the case of manganous salts the oxidation can be carried beyond the stage of peroxide by digestion on a water-bath for some time, when a pink solution of permanganic acid or of alkaline permanganate is slowly formed. In the 1901 paper he writes:—"Recently I discovered that the presence of a trace of silver salt has a remarkable effect on persulphate solutions, greatly accelerating their oxidising action, and apparently, in some cases, bringing about oxidations which would not otherwise occur. . . ." "Such actions seem to depend on the formation and decomposition of silver peroxide."

"This method of oxidation appeared as if it might be suitable for the conversion of manganous salt into permanganate, and experiments confirmed this view. Minute quantities of manganese could be quite easily detected by gently warming the solution with persulphate in presence of sulphuric or nitric acid, and with addition of a drop of dilute silver nitrate solution."

The delicacy of the test was found to be such that 0.001 mgrm. could still be detected by it when the total liquid amounted to about 0.5 cc.

In regard to carrying out the test Marshall states that

"only a minute quantity of silver salt should be employed, otherwise there may be separation of finely-divided silver peroxide; it is not advisable to boil the liquid, but rather to allow it to stand for a little at a moderate temperature. . . ."

In the concluding paragraph of the paper he adds that "the reaction could apparently be employed colorimetrically for quantitative purposes. This was tested roughly as follows." 5 cc. of a solution containing 0.05 mgrm. of manganese as manganous sulphate were oxidised by the method described; 5 cc. of a solution containing 0.05 mgrm. of manganese as potassium permanganate were acidified, and both solutions were made up to the same volume. "When placed in similar tubes the two solutions showed no appreciable difference as regards depth of colour."

A few months after the publication of this paper there appeared a paper by Walters (*CHEMICAL NEWS*, 1901, lxxiv., 239) on "Ammonium Persulphate as a Substitute for Lead Peroxide in the Colorimetric Estimation of Manganese," in which the following passages occur:—

"Almost everybody who has used lead peroxide in the colorimetric estimation of manganese has wished for a substitute which would dissolve completely in the acid solution, thereby allowing the comparisons to be made as soon as the solutions are cool. In the former method it is necessary to use a centrifugal machine or allow considerable time for the finely-divided lead to settle. The substitute should be as cheap (or nearly so), act as rapidly, and be fully as accurate."

"The writer has made a few experiments in the past with different substances, but without success, until, acting on a suggestion of Mr. Hugh Marshall's which appeared in the *CHEMICAL NEWS* (lxxxiii., 76), that ammonium persulphate could probably be used for the quantitative estimation of manganese colorimetrically."

The author goes on to mention that the silver nitrate is essential, but that the quantity must be small or silver peroxide is formed which interferes with the colour; also that solution of ammonium persulphate, especially in presence of silver salt, is very rapidly decomposed. He then gives some details relative to the application of Marshall's persulphate method as a quantitative method for determining manganese in steels, pig-irons, and blast-furnace cinders, dealing with suitable quantities of these substances to employ, suitable quantities of silver nitrate and of ammonium persulphate to be used, heating, &c. He also adds some illustrative quantitative results.

With respect to the impression conveyed by this paper it must, in the first place, be clearly pointed out that Marshall's connection with the reaction did not merely consist in throwing out a "suggestion" that ammonium persulphate could "probably" be used for the quantitative estimation of manganese colorimetrically; on the contrary, from the evidence of his own qualitative experiments, Marshall was led to state the opinion that "the reaction could apparently be employed colorimetrically for quantitative purposes," and on putting the matter to the test of experiment he found this opinion to be confirmed. In the second place, the several points referred to above as having been mentioned by Walters in connection with the carrying out of the test do not—apart from the details of the particular adaptation—involve any features to which attention had not already been directed by Marshall. Any new matter in Walters's paper as compared with Marshall's consists in the details of the application of the test—already described in all essentials—to the special purpose in hand.

In view of the foregoing facts it may be fairly claimed that the test should be described as Marshall's test, and should not be connected with the name of Walters as if the latter were its author. This has not been the usual practice, however, and although Holland (*CHEMICAL NEWS*, 1907, xcvi., 3) and Schowalter (*Zeit. f. Unters. Nahrung. u. Genussmittel*, 1914, xviii., 553) correctly credit the reaction to Marshall, numerous writers of text-books and papers, unaware, doubtless, of the actual facts of the matter, have incorrectly attributed the authorship to

Walters (see, for example, Hillebrand, "The Analysis of Silicate and Carbonate Rocks," 1910, p. 117; Washington, "The Chemical Analysis of Rocks," 2nd Edition, 1910, p. 167; Mellor, "Quantitative Inorganic Analysis," 1913 i., 382; Williams, CHEMICAL NEWS, 1909, xcix., 288; Boyle, *Journ. Ind. and Eng. Chem.*, 1912, iv., 203).

Two cases may be quoted in which the misapprehension appears very clearly:—

Stehman (*Journ. Am. Chem. Soc.*, 1902, xxiv., 1204) begins a paper on "The Determination of Manganese in Iron and Steel" with the words:—"Walters has shown that ammonium persulphate in the presence of a small amount of silver nitrate can be employed to advantage in place of lead peroxide, for the oxidation of manganese in the colorimetric method."

Again, Schmidt (*Journ. Am. Chem. Soc.*, 1910, xxxii., 965) in a paper on "A Colorimetric Determination of Manganese in the presence of Iron," describes the employment of the reaction for determining manganese in pharmaceutical preparations such as peptonates, syrup of hypophosphites, &c. He says:—"No originality can be claimed for the method, as it was proposed several years ago by Walters. . . ." "The determination depends on the power of the persulphates to convert bivalent manganese into permanganic acid in the presence of silver nitrate."

In view of what has been stated in the foregoing, is it too late to plead that chemists who have occasion to mention or to write about these two manganese reactions should connect them with the names of the actual authors?

THE INFLUENCE OF COMPOSITION UPON THE CORROSION OF STEEL.*

By LESLIE AITCHISON, M.Met.

(Continued from p. 130).

PART III.

Microscopic Evidence of the Influence of Composition on the Corrosion of the Steels.

AFTER the chemical analysis of a steel, nothing is of greater importance than its microstructure. The various changes in composition of steels are reflected completely in the microstructure, and not only the composition but also the heat treatment. In the series of steels under consideration no attempt has been made to vary the heat treatment; in all cases they have been normalised at 900° C., but this does not mean that they are all in the same condition with reference to heat treatment. The various thermal equilibrium diagrams of the different systems of ternary alloys necessitate that this slow heating to 900° C., followed by a normal cooling, should produce different types of structure in the different steels (quite apart from chemical composition as such) depending upon the position of the change points, &c. This of course is no disadvantage for the purpose in hand, since the different types of structure that are produced have each their quota of information to provide.

It is almost a platitude to say that from the chemical composition of a steel alone it is impossible to forecast the resulting microstructure, and certainly from the microstructure nothing but an extremely wide experience and a good guess will enable an observer to estimate the chemical composition. Certainly, the actual structure of steels of one type are fairly uniform—e.g., the high tungsten series show a regular change, each of which might have been foretold had the structure of the steels above and below been known, but to distinguish between a high tungsten and a high chromium steel simply by the microstructure would be next to impossible, both being in the region productive of solid solution and excess carbide ;

yet these two structures, so singularly alike, give entirely different results when corroded.

Structural Details to be Considered.—Amongst the points to be considered the actual constituents present in the steels of the series are of primary importance. In the series of steels involved in these experiments the majority of the constituents found in steels are to be met with. The plain carbon steels have of course ferrite, cementite, and pearlite. The latter constituent is found in various of the forms in which it is generally encountered, passing from the ordinary, rather jumbled pearlite of a normal steel, and which is found uniformly throughout the plain carbon steels, to sorbitic pearlite (which is found usually in manganese steels) on the one hand and to the almost entirely segregated ferrite and cementite on the other. This latter variety is found in the nickel steels containing the lower percentage of carbon. It might be inferred quite naturally that such diverse structures would produce quite different results under the influence of the corrosion media.

Pearlite is also found in a large number of the other steels: broadly in all those with less than 4 per cent of the third constituent. In these steels the pearlite is usually of the small variety, the cementite being in small globules dotted about the ferrite rather than the laminae more generally observed. As the carbon or the percentages of the third element increases the excess of carbide shows itself in a quite free form; this is in general accompanied by the substitution of solid solution for pearlite in the structure.

These carbides, an account of which may be found in the various papers of Arnold and Read (*Journ. Iron and Steel Inst.*, 1910, I., 169; 1911, I., 249; 1912, I., 215; and *Journ. Mech. Eng.*, 1914, I., 223; 1915, I., 247), are of widely different compositions but of considerable similarity of properties. Usually they appear in one of three forms—as part of the pearlite, as boundaries to the grains of solid solution, or as globules dotted about throughout the solid solution, with apparently no relationship to the boundaries of the grains. In all cases they are found as pure white constituents after treatment with ordinary etching reagents. The stability of these carbides under attack is of some importance in connection with the corrodibility of steels. Naturally this stability varies very much with the nature of the attacking medium (c.f. attack of 3 per cent sodium chloride solutions and 10 per cent sulphuric acid upon steel No. 27). In this connection some information can be gleaned from the papers of Arnold and Read cited above.

The solid solutions on the whole are not structureless, but exhibit a small stippled appearance (this is seen in Figures 7 and 10 of Part I.). An exception to this is found in the highest vanadium steel. In one of the steels (the highest cobalt steel, No. 66) a portion of the carbide has decomposed into ferrite and graphite. This is not an uncommon experience with certain steels, particularly if annealed. The nickel steels with about 0.8 per cent of carbon are particularly prone to this precipitation. The result in the cobalt steel is that there is graphite lying enclosed as the kernel of a nut of solid solution of cobalt in iron.

Throughout the series the grain size varies with the composition, the pure carbon steels having usually larger grains than the alloy steels. In the steels with only a small proportion of the third element this change in grain size is slight or nil, except in the 3 per cent tungsten series, but the large proportion of tungsten or chromium or vanadium has produced a noteworthy difference (c.f. Figures 7 and 8). The series employed does not contain any steels showing troostitic or purely austenitic structures.

The question of mechanical strain due to either working or thermal treatment does not enter seriously into these steels, any strain resulting from the previous treatment of the steel having been eliminated from them as far as possible by the normalising at 900° C. Some thermal strain

* A Contribution to a General Discussion on "The Corrosion of Metals" before the Faraday Society, December 8, 1915.

must have remained after this cooling, but only such as is inherent to the cooling of all steels. A little mechanical strain is also bound to have been produced during the turning and polishing of the specimens, but this is almost unavoidable. (This aspect of the question has been dealt

very little carbide). In particular this has been dealt with by Humfrey ("Carnegie Memoirs," Iron and Steel Institute, 1913, 86) and by Rosenhain and Ewen (*Journ. Inst. Metals*, 1912, II., and 1913, II.). Both of these authors agree that the material is amorphous, but give

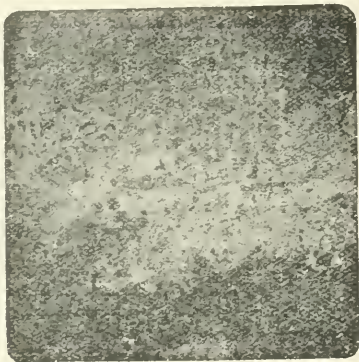


FIG. 2.—C 0.07, Ni 3.07.

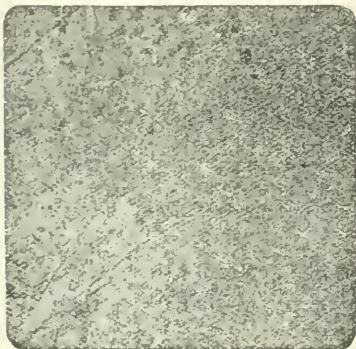


FIG. 3.—C 0.88, Ni 2.97.

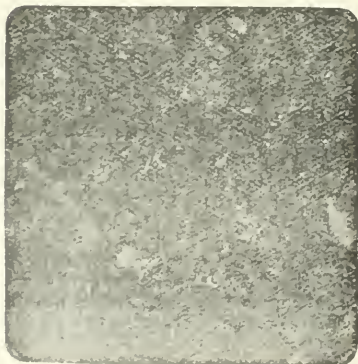


FIG. 4.—C 0.07.

with by various workers; cf. Heyn and Bauer, *Journ. Iron and Steel Inst.*, 1909, I., 159).

Besides these factors that may enter into the corrosion effects two others must be considered. The first of them is the inter-crystalline or inter granular material found in various of these steels (e.g., those containing any large quantity of ferrite and those with much solid solution and

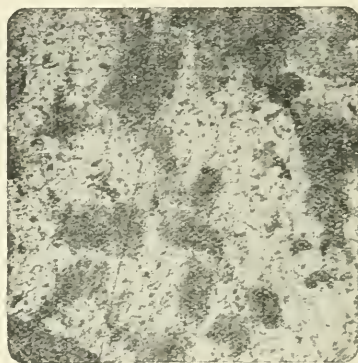


FIG. 5.—C 0.72, Co 20.85.

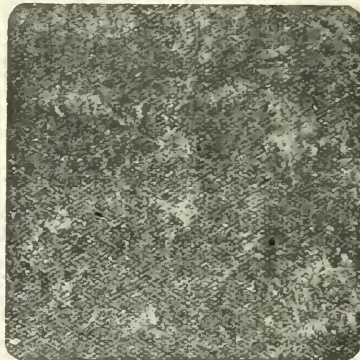


FIG. 6.—C 0.89.

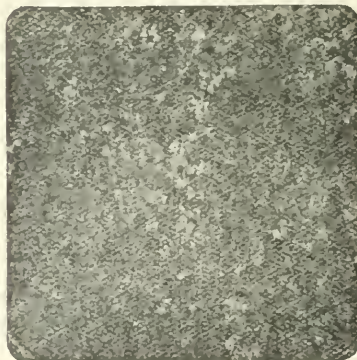


FIG. 7.—C 0.38, V 0.22.

different explanations of its formation. Humfrey maintains that these inter-granular volumes represent those portions of the mass where the regular arrangement of the molecules due to the orientation of one crystal is being gradually (more or less) changed to the different, orderly arrangement due to the orientation of the adjacent grain. On the other hand, Rosenhain and Ewen express the

opinion that the space is simply filled up by excess matter from the crystals when the distance between the crystals has become too small for a continuation of a crystal growth in accordance with the orientation of the surrounding grains. Whichever or whatever explanation be accepted as the cause of this amorphous layer, its presence can hardly be doubted and its influence upon the corrosion cannot be neglected. The second remaining factor that may influence the behaviour of the steel when corroded is the possibility of twinning in the solid solution. This is usually confined to those materials possessing some grains of pure solid solution and no other constituent which can influence the growth of that particular grain. This structure was not apparent in any of the steels of the series, but one other containing approximately C 1.2 per cent, Mn 12 per cent, Si 0.35 per cent, S 0.03 per cent, P 0.06 per cent, and showing this type of structure, has been corroded in the manner described below.

Manner of Experiments and Results Obtained.

The sections taken from the bars after their normalisation were polished in the usual way upon emery cloth and paper and finished with diamantine powder upon moist, rotating selyvt cloth. They were then dried with absolute alcohol and washed with ether. When quite clean and dry they were immersed in a solution of 3 per cent sodium chloride, being placed on the bottom of a glass crystallising dish. After being immersed and left quite undisturbed in the dark for ten days they were removed and washed in a gentle stream of tap-water, dried with absolute alcohol, and examined under the microscope.

The results obtained show the utmost regularity. As might be expected, the ferrite is attacked in every steel of the series, though of course not to the same extent. It is fairly safe to assume that in every case the early stages of the attack are accompanied by the production of etching pits or their counterparts. This is well seen in the nickel steels Nos. 54 and 57 (Figs. 2 and 3). In the bar iron which had been melted to remove the slag and which had only 0.07 per cent of carbon almost the whole is ferrite, and the attack upon it may be seen in Fig. 4. This shows quite well that the different grains of ferrite corrode to an entirely different extent. The small white dots scattered sparsely over the field are cementite, and being segregated allow the material to act practically as though carbon-free. From the figure it is plain that some grains have not been attacked at all, whilst others have been subjected to the attack of etching pits, which have developed and deepened during the attack. In all those that have been attacked there is a rough or stippled appearance, showing the unevenness of the result of the attack in that particular grain, quite different from the appearance produced during an ordinary etching. The cobalt steel that contained some graphite has produced some ferritic material (containing cobalt of course), and the attack on this may be seen in Fig. 5. Here the attack in the ferrite has been rather "patchy," and the boundaries of the grains are not at all so well marked as in the bar iron.

Curiously enough the pearlite in practically every steel under review is corroded so that it is practically indistinguishable from the ferrite. This is well seen in Fig. 6 (which is steel No. 10, containing 0.89 per cent of carbon). It is hardly possible to pick out the boundaries of the grains in this steel, and in the grains themselves the attack is such as to leave no traces of the cementite, everything having been attacked. This is the result throughout the list of steels, it being next to impossible to distinguish any of the steels below 0.9 per cent of carbon from one another. It also holds for the various alloy steels that contain pearlite. Fig. 7 (No. 39, having 0.38 per cent of carbon and 0.22 per cent of vanadium) shows no cementite of the pearlite still standing, but shows a preferential attack of some grains over the others. It is almost impossible to distinguish between ferrite and pearlite in this steel (as in the others). In the steels greater than 0.9 per cent of carbon there is the same kind

of attack, but rather intensified, the structurally free carbide having apparently helped the action considerably. This is seen very well in Figs. 8 and 9, representing steels Nos. 9 and 42, having respectively 1.46 per cent of carbon and 1.30 per cent of carbon, with 0.21 per cent of vanadium. The second case (Fig. 8) has probably more remnants of the pearlite structure than any other steel in the series. Fig. 12 (*infra*) also shows very clearly some of this remaining pearlite structure.

(To be continued).

THE PRODUCTION OF CHLOROPICRIN BY THE ACTION OF AQUA REGIA ON ORGANIC COMPOUNDS.

(PRELIMINARY PAPER).

By RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE,
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AQUA regia has been found to be a chlorinating (Datta and Fernandes, *Journ. Am. Chem. Soc.*, 1914, xxxvii, 1007) as well as an oxidising agent (Datta, *Ibid.*, 1914, xxxvi, 1011). It has now been found that it sometimes acts destructively, leading to the rupture of organic substances subjected to its action, with the production of chloropicrin. The transformation into chloropicrin is quantitative in some cases, in others it takes place to a limited extent, while in some cases it does not take place at all. The action of aqua regia on the following substances has been studied.

Acetone.—Aqua regia decomposes acetone almost quantitatively into chloropicrin, and the reaction can therefore be employed as the best method for the laboratory preparation of this substance. Hofmann (*Ann.*, 1866, cxxxix., 111) gave a laboratory method for the preparation of this compound by the action of bleaching powder on picric acid. This procedure, however, gives only poor yields, and is troublesome to carry out.

To a mixture of 2 parts of nitric acid and 3 parts of hydrochloric acid, acetone is gradually added, the acid mixture being warmed slightly. An oil separates at first, which soon dissolves with the production of the characteristic odour of chloropicrin. The addition of acetone is stopped when a quantity equal to a tenth part of the acid mixture has been added. When the whole of the acetone has been added the mixture is warmed on the water-bath for some time to enable the reaction to become complete. The resulting liquid is next subjected to steam distillation, and the compound is separated, dried by means of calcium chloride, and finally distilled at a slightly reduced pressure.

The substance boiled between 113–114° at about 750 mm. The yield obtained was 85 per cent of the theory. To establish its identity a chlorine determination was made.

0.1661 gave 0.4288 AgCl. Calculated for CCl_3NO_2 —Cl, 64.74; found, 63.86.

It has been observed that if the reaction is carried out in the cold, with very gradual addition of acetone, an oil containing chloropicrin separates, which, on slow evaporation in a desiccator, yields colourless crystals having m. p. 103–104°. This is being investigated.

Allyl Alcohol.—The action of aqua regia on allyl alcohol was next studied, inasmuch as it contains an unsaturated bond. When the reaction was carried out with warming, quantitative production of chloropicrin was the result; but when it was carried out in the cold a mixture of chloropicrin and another substance which is under investigation was produced. Allyl alcohol was gradually added to a mixture of the acids (2:3), with occasional warming on the water-bath. Its transformation into chloropicrin was complete. The resulting solution was subjected to steam distillation. A colourless oil was obtained which was identified by distillation as usual.

Ether.—When ether was added in small portions to aqua regia no change was apparent at first, but on warming limited action took place. At the end of the reaction no oil was deposited, a pungent odour of chloropicrin being noticed as usual. The product was separated by steam distillation, and it was found that a very small quantity of chloropicrin had been formed.

Ethyl Alcohol.—Ethyl alcohol is decomposed only partially with the formation of chloropicrin. To a mixture of nitric and hydrochloric acids (2:3) ethyl alcohol was added in small quantities. At first no reaction took place, but after a time the action became violent and the acid mixture had to be cooled. After the action had subsided the mixture was warmed on the water-bath for a few minutes. The chloropicrin was recovered as usual after steam distillation.

Methyl Alcohol.—Methyl alcohol remains undecomposed by aqua regia even on warming on the water-bath, and hence no chloropicrin is produced. After a very prolonged action only a slight smell of chloropicrin could be noticed.

Formic and Acetic Acids.—These acids are quite stable and remain undecomposed even on warming. Consequently, no chloropicrin is formed in these cases.

A host of other substances has been found to give chloropicrin as the ultimate decomposition product, and it appears that the production of chloropicrin might be quite general. Investigations to establish this as well as a general study of the action of aqua regia and also the action of nitric acid, in conjunction with bromine and iodine, on organic bodies are being continued.—*Journal of the American Chemical Society*, xxxvii., No. 3.

THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES.*

By ROGER C. WELLS.

INTRODUCTION.

Scope of the Investigation.

THE experiments described in this bulletin were made to aid in elucidating the chemistry of ore deposition. They were confined to aqueous solutions at moderate temperature, and they have shown the order of solubility of the compounds of each of the classes investigated—sulphides, hydroxides, carbonates, and silicates. The solubility of most of these compounds in water is so slight that its direct and accurate determination is difficult. The literature of the subject accordingly contains many determinations of their solubility by indirect physicochemical methods, and some of these are given in this bulletin in order that they may be compared with the results obtained in the experiments here reported. Three or four complications have been met in the otherwise simple relations of solubility—namely, that sulphides may act as reducing agents, that carbonates and silicates may precipitate hydroxides, and that solids may require considerable time to assume their most stable forms.

Considered chemically the precipitation of an ore from a solution may require only a single condition: the constituents of the ore must be present in the solution in certain forms and in concentrations above certain minima. A closer examination of this requirement, however, shows that it is conjoined with other minor requirements, all more or less related in such a way that a certain lack of one may exist if another is more than fulfilled. A statement of the relative solubility of two metallic compounds based on the final table given in this paper need not, for example, correspond with the order of their deposition in nature, although the solubility of an ore has a direct relation to its deposition. The solubilities presented were

determined by starting with solutions containing the competing metallic constituents in equal concentrations, whereas in nature the constituents occur in various concentrations, and the deposition of ores is governed very largely by the mass law, a point that will be more fully discussed elsewhere in this bulletin.

The present experiments do not show the behaviour of solutions that may exist in magmas or that may constitute magmatic exudations. Such solutions are not only at high temperature and pressure, but some of them are also supposed to contain liquid carbon dioxide, chlorides, fluorides, and sulphides, together with water. As some of these compounds are mutually incompatible, the assumption that such solutions are a source of ore deposits requires a great deal of explanation, one of the first requirements being the ascertainment of groups of metallic and non-metallic elements that can be appreciably compatible in such solutions. Though such solutions seem to have played important roles in the deposition of certain ores, as indicated by geologic evidence, yet, as aqueous solutions at moderate temperatures form not only the solvent but the transporting medium and distributing agent of enormous quantities of metalliferous material, especially in the upper parts of the earth's crust, any generalisations that may be established with reference to such solutions will have wide application.

It is interesting to trace the cyclic courses of the various elements in the numerous operations that are going on unceasingly in the earth. The continents are elevated and eroded, the sediments consolidate and possibly fuse together anew to form new magmas, intrusions and extrusions are constantly occurring. The following quotation from T. Sterry Hunt well expresses the continuity of these processes ("Chemical and Geological Essays," 1878, xii., 235):—

"We learn . . . that amid all the changes of the face of the globe the economy of nature has remained the same. We are apt, in explaining the appearances of the earth's crust, to refer the formation of ore beds and veins to some distant and remote period, when conditions very unlike the present prevailed, when great convulsions took place and mysterious forces were at work. Yet the same chemical and physical laws are now as then in operation—in one part dissolving the iron from the sediments and forming ore beds, in another separating the rarer metals from the ocean's waters, while in still other regions the consolidated and buried sediments are permeated by heated waters, to which they give up their metallic matters, to be subsequently deposited in veins. These forces are always in operation, rearranging the chaotic admixture of elements which results from the constant change and decay around us."

The courses of the valuable metals in these cycles, as well as those of the non-metals most frequently associated with them, are of particular significance in respect to theories of ore deposition.

In discussions of the origin of ore deposits the non-metallic constituents are frequently neglected. If an ore contains more than one element the term "source of the ore" is equivocal, as it is possible that the metal may have come from one source and the non-metal from another. The presence of the non-metallic constituent needed to precipitate the metallic constituent may in fact explain the presence or absence of an ore at a given locality. Moreover, the proportion of such a constituent may determine the character of the ore; for example, in a solution containing iron and sulphur an excess of sulphur may yield pyrite and an excess of iron may yield pyrrhotite. This essential factor must be borne in mind in considering the mode of formation of ores. In the treatment adopted in this bulletin the constituents discussed are primarily arranged according to the non-metallic constituent that combines with the metal, the sulphides in one group, the carbonates in another, and so on; that is, all the possible compounds of each metal are not considered together. Both arrangements have advantages,

* Bulletin 609, United States Geological Survey.

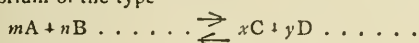
The one adopted here is at least equal in value to that followed in the older method of studying all the salts of one metal together.

In making a laboratory investigation it may happen that the methods employed do not reproduce natural conditions closely. For instance, in studying the behaviour of gold, platinum, and silver, soluble salts are used in the laboratory, whereas in nature soluble salts are rarely found, and the essential problem is to determine the conditions of solution and transportation of those metals rather than their precipitation. Frequently, however, the assumption is warranted that mixtures of soluble metallic salts in noteworthy concentrations may come under the influence of precipitating agents, such as sulphides, sulphates, carbonates, and hydroxides, and be in part or completely precipitated. The precipitating action of solids will differ from that of solutions only in respect to the concentration of the precipitant available and the rate of the action, the action approaching that of an extremely dilute precipitant in solution.

In considering precipitation several elemental concepts have wide applicability, such as the law of mass action, ionisation, and the constant solubility product. For the benefit of those who may not have access to detailed treatises on these subjects it seems appropriate to explain these concepts briefly in so far as they are applicable to the present investigation, an investigation of solutions in which partial precipitation occurs. The law of mass action accounts for the equilibria occurring in the solution, the ions determine in the most general way the properties of inorganic solutions, and solubility finds its best interpretation through the solubility product.

The Mass Law.

The law of mass action has very wide application. Suppose that in any homogeneous system at a definite temperature there is possible a general reaction or equilibrium of the type—



then, according to the law of mass action,

$$K = \frac{c^x d^y}{a^m b^n} \dots\dots$$

where a , b , c , d represent the concentrations of the molecular species A , B , C , D , and K is a constant, the equilibrium constant. It follows from this relation that an increase in the concentration of any substance on one side of the equation must result in an increase in the concentration of the substances on the other side and a decrease in the concentration of the other substances on the same side.

(The sign $\rightleftharpoons$ indicates that the reaction may occur in either direction, according to conditions, and, according to the usual interpretation, equilibrium is merely the condition attained when the rate of the two opposing reactions is equal).

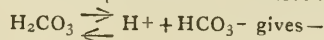
Ions and the Solubility Product.

This is not the place to present arguments for and against the theory of electrolytic dissociation suggested by Arrhenius in 1887. Almost every recent work on chemistry shows abundantly the fruitfulness of the conception of ions and presents the generalisations based on it. (For example, see Julius Stieglitz, "The Elements of Qualitative Analysis," 1911: The Century Co.). Moreover, the phenomena of electric conduction warrant the assertion that the existence of ions is not only theoretically possible but is practically demonstrated.

The statement that a substance "ionises" in solution does not mean that it ionises completely, but only that its characteristic ions appear among the "molecular species" contained in the solution and are potential factors of chemical reactions. The written symbols for ions indicate the nature of their electric charges—that is, they show whether they are positive or negative; for example,

H^+ , Cl^- , for of course such ions are entirely different from free atoms. Moreover, every solution must contain equivalent numbers of positive and negative ions.

As "molecular species" contained in the solution the ions as well as the molecules may be considered with reference to the mass law. Such a consideration leads to the conception of the "dissociation constant." Thus



$$K = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

the dissociation constant for the primary dissociation of carbonic acid.

With respect to chemical precipitates it was early assumed that the concentration of the non-ionised dissolved portion is not changed by the presence of other salts (A. A. Noyes, "Ueber die gegenseitige Beeinflussung der Löslichkeit von dissociierten Körpern," *Zeit. Phys. Chem.*, 1890, vi., 243), but it has since been discovered that large deviations from this rule may be shown by moderately concentrated solutions (S. Arrhenius, "Ueber die Aenderung der Stärke schwacher Säuren durch Salzzusatz," *Idem.*, 1899, xxxi., 224). The great number of solutions in which it holds fairly well, however, warrants its consideration, especially as it leads to a principle of even wider applicability, namely, that of the constant solubility product.

The solubility product (S.P.) is the product (result obtained by multiplication) of the concentrations of the ions yielded by the precipitate in the solution, which must be exceeded before precipitation can occur. Dr. John Johnston, of the Geophysical Laboratory of the Carnegie Institution of Washington, has suggested to me the need of a simpler term than "solubility product" for the mathematical function under discussion. The words "solubility product" merely denote a number that is a characteristic property of each specific substance. The evaluation of these numbers is one of the constant aims of chemists. There will be as many powers in this product as there are ions formed from the salt under examination. Thus for a uni-univalent salt $S.P. = [B][A]$, in which $[B]$ and $[A]$ are the concentrations expressed as grm. molecules or grm. ions per litre. For univalent salts the solubility product takes the form $S.P. = [B]^2[A]$ or $[B][A]^2$, and so on for more complicated salts.

Therefore if to a precipitate in a saturated solution a salt having a common univalent ion is added, the concentration of the other ion or ions of the precipitate will be decreased. Recent investigations have shown, however, that the effect of the addition of a common bivalent ion is insignificant (A. A. Noyes and W. C. Bray, "The Effect of Salts on the Solubility of Other Salts," *Journ. Am. Chem. Soc.*, 1911, xxxiii., 1648). It is not yet clear whether these results indicate a failure of the theory, or whether, as seems more likely, correct evaluations of the ionic concentrations have not yet been obtained. However, though in many solutions the relations are still considered only qualitatively, the more insoluble the precipitate considered the more certainly the theory appears to be substantiated (W. D. Harkins, "The Solubility of Univalent Salts in Solutions of Salts of Different Types," *Journ. Am. Chem. Soc.*, 1911, xxxiii., 1827). An application of the principle to sulphides, hydroxides, and carbonates of the heavy metals would thus appear not wholly unwarranted, and some applications of it have therefore been made in this bulletin.

Of course it remains true that if a substance with no common ion is added to a solution the solubility of the precipitate is in general slightly increased, for a little of it goes to form every possible new species of molecule by metathesis, and furthermore, the solubility of a substance, even in the presence of a common ion, may be greatly increased under special conditions on account of the formation of complex ions.

(To be continued).

THE ACTION OF THIONYL CHLORIDE ON
SULPHIDES.

By B. NORTH and C. B. CONOVER.

INVESTIGATION of the action of thionyl chloride on inorganic substances has been confined almost entirely to its deportment toward metals, metalloids, and oxides. The action of the reagent on these has been quite exhaustively studied by North and Hageman and described in the *Journal of the American Chemical Society* (1912, xxxiv., 890; 1913, xxxv., 352, 543). Letting M represent a divalent metal of metalloid, reaction follows the general equation $3M + 4SOCl_2 = 3MCl_2 + 2SO_2 + S_2Cl_2$. With oxides, reaction takes place according to the following: $MO + SOCl_2 = MCl_2 + SO_2$. In the case of metals or metalloids having more than one compound with chlorine, the lower chloride is usually, but not always, produced if the metal is in excess. Likewise the higher chloride is formed when the metal is treated with a large excess of the reagent.

The chief difference in the two reactions given above is that with metals or metalloids sulphur monochloride is always one of the products. Sulphur monochloride is not produced in reactions with oxides. In the case of higher oxides or peroxides, reaction does not follow the general equation given above, but always results in the formation of a mixture of chloride, sulphate, and sulphuryl chloride, if an excess of the oxide is used, or chloride, sulphur dioxide, and sulphuryl chloride when an excess of thionyl chloride is employed.

So far as the authors have been able to ascertain, only three reactions of thionyl chloride on sulphides have heretofore been studied. The action on phosphorus pentasulphide was studied in 1858 by Carius (*Ann.*, 1858, cvii., 303), who undoubtedly was the first to prepare thionyl chloride in a pure condition. Carius thought the reaction proceeded according to the equation $P_2S_5 + 5SOCl_2 = P_2O_5 + 5S_2Cl_2$, but in 1884 Prinz found this to be incorrect (*Ann.*, 1884, ccxxiii., 355). According to Prinz the reaction takes place as follows: $-2P_2S_5 + 6SOCl_2 = 4PSCl_3 + 3SO_2 + 9S$. Prinz also tried the action of thionyl chloride on antimony trisulphide, finding that the reaction takes place as follows: $-6SOCl_2 + 2Sb_2S_3 = 4SbCl_3 + 9S + 3SO_2$. Both of these reactions must have been carried out at a temperature lower than 150° , for above this point thionyl chloride and sulphur react according to the equation $2SOCl_2 + 3S = SO_2 + 2S_2Cl_2$.

No further reaction with a sulphide was studied until 1896, when Besson investigated the reaction of this reagent on hydrogen sulphide (*Comptes Rendus*, 1896, ccxii., 467). He found the reaction to proceed according to the following equation: $-2SOCl_2 + 2H_2S = 4HCl + SO_2 + 3S$.

The reactions described in this paper were brought about in sealed glass tubes at a temperature of $150-180^\circ$. With the exception of ferrous sulphide, the sulphides employed were made by precipitation. They were thoroughly dried at 110° , and were preserved in tightly stoppered tubes. In every case sulphur dioxide and sulphur monochloride were formed.

Zinc Sulphide.—When zinc sulphide was treated with thionyl chloride, reaction commenced in the cold, but soon stopped. The sealed tubes containing the material were heated at $150-200^\circ$ for several days without any change in appearance, due to the fact that both the chloride and sulphide are white. When the tubes were opened they were found to contain, in addition to the white solid, considerable sulphur dioxide and sulphur monochloride. The white solid was analysed, and found to be zinc chloride. Reaction proceeds therefore according to the equation $ZnS + 2SOCl_2 = ZnCl_2 + SO_2 + S_2Cl_2$.

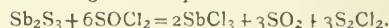
Cadmium Sulphide.—Reaction did not commence in the cold when cadmium sulphide and thionyl chloride were brought together. When the tube was heated at about 200° reaction appeared to take place slowly, as indicated by the very gradual change in colour from yellow to white.

After being heated for about fifteen days, the solid contents of the tube appeared entirely white. Analysis showed this compound to be cadmium chloride, hence reaction proceeds as follows: $-CdS + 2SOCl_2 = CdCl_2 + SO_2 + S_2Cl_2$. The tube also contained much sulphur dioxide and sulphur monochloride.

Silver Sulphide.—Thionyl chloride did not react with silver sulphide in the cold. After heating for several days the sulphide was found to have changed into silver chloride, as was shown by subsequent analysis. The action of thionyl chloride on silver sulphide proceeds according to the equation $Ag_2S + 2SOCl_2 = 2AgCl + SO_2 + S_2Cl_2$.

Arsenic Sulphide.—Arsenic sulphide was found to react readily with thionyl chloride at 150° , going completely into solution. Inasmuch as thionyl chloride and arsenic chloride are both liquids and miscible, it was supposed that reaction had taken place with the formation of the latter compound according to the equation $As_2S_3 + 6SOCl_2 = 2AsCl_3 + 3SO_2 + 3S_2Cl_2$. The liquid in the tube was therefore a mixture of arsenic trichloride, sulphur monochloride, and the excess of the thionyl chloride. This liquid was fractionated in an attempt to bring about a separation, but on account of the small amount of material a complete separation was impossible. A small amount of distillate was obtained at a temperature above 126° . This had a very pronounced odour of sulphur monochloride, and when decomposed in water gave a precipitate of sulphur. The solution gave a strong test for arsenic, hence the authors are of the opinion that reaction took place according to the equation given, and that the distillate obtained above 126° was a mixture of arsenic trichloride and sulphur monochloride.

Antimony Sulphide.—Antimony sulphide reacts readily with thionyl chloride at a temperature of $150-200^\circ$, giving the trichloride, sulphur dioxide, and sulphur monochloride according to the equation—



This reaction was studied by Prinz in 1884, and was found by him to result in the formation of a mixture of trichloride, sulphur monochloride, and sulphur. Prinz must have carried out this experiment below 150° or without excess of thionyl chloride, inasmuch as the latter reacts with sulphur at 150° to give sulphur dioxide and sulphur monochloride.

Ferrous Sulphide.—The sample of ferrous sulphide employed was the crude article such as is used for the preparation of hydrogen sulphide. An analysis of the powdered sample for iron and sulphur showed a slight excess of the latter. This would not interfere with the reaction, however, inasmuch as sulphur itself reacts with thionyl chloride, giving sulphur dioxide and sulphur monochloride.

The iron sulphide and thionyl chloride were heated together at 150° . Reaction took place readily with the formation of bright green hexagonal plates which, by transmitted light, were ruby-red. Analysis proved these to be ferric chloride, $FeCl_3$. Reaction took place according to the equation $6FeS + 16SOCl_2 = 6FeCl_3 + 8SO_2 + 7S_2Cl_2$. A small amount of light coloured insoluble matter, probably silica, was obtained when the sample was dissolved in water for analysis. This was collected on a Gooch crucible, dried and weighed, and the weight deducted from the weight of the sample.

This reaction differs from the others studied, inasmuch as the ferrous sulphide was oxidised to the ferric state. No indication of ferrous chloride was found.

Copper Sulphide.—Upon heating copper sulphide with the reagent at 150° , reaction took place within a few hours with the formation of a dark brown solid substance. This was analysed and found to be anhydrous copper chloride. Reaction therefore took place according to the equation $CuS + 2SOCl_2 = CuCl_2 + SO_2 + S_2Cl_2$.

Stannic Sulphide.—The material used for this experiment was the ordinary mosaic gold, made in the dry way. After heating for six hours at 150° no apparent change had taken place. The tube was then heated for a number

of days at a temperature of from 150—200°, after which it was noticed that a considerable portion of the sulphide had dissolved. When the tube was opened sulphur dioxide was evolved. Furthermore, the odour of sulphur monochloride was very prominent. Considering this, together with the fact that the compound used was a compound of tetravalent tin, the authors are of the opinion that reaction proceeds slowly with the formation of tin tetrachloride according to the equation $\text{SnS}_2 + 2\text{SOCl}_2 = \text{SnCl}_4 + 2\text{SO}_2 + 2\text{S}_2\text{Cl}_2$. The liquid in the tube was probably a mixture of tin tetrachloride, sulphur monochloride, and the excess of thionyl chloride. An attempt was made to fractionate this, but it was a failure, due to the small amount of material at hand.

Mercuric Sulphide.—Mercuric sulphide was found to react readily with thionyl chloride at 150° with the formation of long needle crystals of mercuric chloride. Reaction proceeds according to the equation $\text{HgS} + 2\text{SOCl}_2 = \text{CuCl}_2 + \text{SO}_2 + \text{S}_2\text{Cl}_2$.

Summary.

Thionyl chloride reacts with sulphides according to the following equation, in which M represents a divalent metal: $\text{MS} + 2\text{SOCl}_2 = \text{MCl}_2 + \text{SO}_2 + \text{S}_2\text{Cl}_2$. With sulphides as with oxides and metals, thionyl chloride seems to show a selective action, reacting much more readily with some than with others.—*Journal of the American Chemical Society*, xxxvii., No. 11.

LATEST COKE RECOVERY PLANT INSTALLATIONS.

A VERY complete and modern plant has been installed at the Normanby Park Steelworks, Yorkshire, for the making of coke, tar ammonia, and benzol. The buildings are of the latest planning in ferro-concrete on the Mouchel-Hennebique system, and there are, in addition to an immense washery, two batteries of 48 regenerative coke ovens of the Semel-Solvay type capable of dealing with 3000 tons of coal per week. Power for operating the plant is supplied by gas engines using blast-furnace gases. The main washery building measures 65 feet long by 40 feet wide, two-thirds of it being 77 feet high and the remaining third rising in the form of a tower 94 feet high, surmounted by a ferro-concrete water-tank with a storage capacity of 62,000 gallons. Designed on the skeleton system, the building is supported entirely on a series of ferro-concrete columns with extended bases, distributing the entire load of the structure and its contents at the rate of 1½ tons per square foot.

The coking ovens are supplied with washed coal at any required rate up to 100 tons per hour by means of conveyor bands connected to a runway, under which charging machines receive and stamp the slack into compression boxes. Each of the 96 ovens carbonises 50 tons of washed coal per week, the stamped slack being fed into the ovens by charging machines. The coke is pushed out through quenchers to an inclined hearth, over which it passes to 36-inch tray conveyors delivering the product to a central screening station and thence to the blast furnaces. Gases from the ovens are collected into a large main and exhausted through air and water condensers, thence passing through tar extractors and scrubbing washers for absorption of benzol and remaining ammonia. After this treatment the gases are utilised, half for heating the flues in the coke ovens and the other half in the steel works. Tar ammonia liquor and benzol extracted from the gases are treated in buildings situated between the coal washery and the batteries of coke ovens.

Another up-to-date plant is the Otto Direct Recovery coke-oven plant, just installed at Teams, in County Durham. This introduces all the best features of recent date. There are two batteries of 60 ovens each, these

ovens being 30 feet long, 7 feet high, and 20 inches wide. The crushed coal is charged into the ovens through openings in the crown from small hoppers, which carry it on rails from the storage bunkers. When carbonisation is concluded the coal is discharged by electrical-driven rams on to a sloping bench and quenched with water. The hot crude gases, after passing through the ram, travel in succession a long horizontal pipe and an atmospheric cooler. They then go to the tar extractor, where they are met by a large volume of hot tar and liquor forced in under pressure. The gas freed from tar passes into the saturator, where the ammonia combines with hot dilute sulphuric acid, forming ammonium sulphate. The sulphate passes through a receiver, where it is separated from any liquor, and then through a centrifugal dryer, while the gas goes on to the bottom of the naphthalene extractor and spray cooling tower. Thereafter the gas is driven through an exhauster, then through a second water cooler, where the last traces of naphthalene are deposited, and afterwards to the benzol tower scrubbers, where it is washed with an oil which removes benzol by a process of simple solution. On leaving the scrubbers about one-half the debenzolised gas is returned to the ovens and used for heating purposes. The crude benzol is subsequently rectified in another portion of the building.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 9, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"*The Distribution of Intensity in Broadened Spectrum Lines.*" By Prof. J. W. NICHOLSON and T. R. MERTON.

1. Using a neutral tinted wedge the actual distribution of intensity in broadened spectrum lines can be accurately measured.

2. With this arrangement quantitative measurements of the hydrogen line H_α have been made, and quantitative observations of other lines of hydrogen, helium, and lithium.

3. The intensity-distribution of lines, broadened by condensed discharges and at high pressures, does not follow the well known probability law known to obtain under certain specified conditions.

4. The broadening of H_α is symmetrical.

5. The most general characteristic of all the curves obtained is that their curvature is away from the axis perpendicular to the wave-length scale.

6. The existence of more than one component accords with the view that electrical resolution of lines is the origin of their broadening.

7. On the supposition of several components symmetrically distributed about the centre, the only general law consistent with the distribution of curvature is that of a sum of linear exponential terms, one for each component.

8. It is shown that under these circumstances discontinuities in the slope of the curves must occur. Those found in the curve for H_α are in quantitative accordance with those expected from available data with respect to electrical resolution.

9. Quantitative observations of H_β , H_γ , and the diffuse series of helium and lithium confirm the view that electrical resolution is the principal cause of the phenomena.

"*Prof. Joly's Method of Avoiding Collision at Sea.*"

By Prof. H. C. PLUMMER.

This brief note adds nothing to the general principle on which Prof. Joly's method is founded, but aims at greater simplicity both in idea and practical detail by introducing the relative speed of the two ships.

The speed and course of an approaching ship being communicated by wireless, the relative speed is easily obtained without calculation by a combination of scales, which is in fact identical with Prof. Joly's collision predictor. The one ship may then be considered stationary, and the locus of the approaching ship at successive signals becomes a series of concentric circles. In the case of impending collision the rate of approach is a maximum along a radius and equal to the relative speed.

Two methods are suggested for comparing the indications of the signals as received with this critical speed, the one involving the use of two direct-reading scales, the other an equivalent arithmetical operation of the simplest kind.

"Apparatus for the Determination of Gravity at Sea."
By Prof. W. G. DUFFIELD.

The development of the form of apparatus as finally adopted is described. It depends upon balancing a column of mercury against the pressure of a constant volume of air contained in a bulb.

The whole apparatus is maintained at as constant a temperature as possible. The height of the column varies inversely as the value of gravity. In an early form of the apparatus the adjustment of the air volume was made by raising or lowering, by means of a magnet, an iron needle immersed in the mercury in the upper part of the apparatus. This lowered or raised the level of the mercury in the vertical tube and produced the change in pressure necessary to restore the lower surface of the mercury to its normal level. The value of gravity was measured by the length of the needle immersed.

A practical difficulty in regulating the position of the needle led to the adoption of a different method of adjustment. In this case the level of the mercury in the lower line was regulated by introducing or extracting mercury through two side tubes, one of which was of coarse bore for making the initial adjustment and the other of fine bore for purposes of delicate measurement. A high sensitivity could be attained by making the diameter of this tube small and that of the vertical tube large. A small pump was used for extracting the mercury.

The constancy of volume was indicated by electrical contact between the mercury and a pointer, a trembling coil and telephone completing the circuit. An arrangement for reducing the effect of temperature variations is described.

The apparatus was tested on a voyage to Australia and modified in accordance with experience gained. It was further tested during part of a return voyage under very unfavourable conditions; nevertheless the results indicate the suitability of this type of instrument for future observations of gravity at sea.

PHYSICAL SOCIETY.

Ordinary Meeting, March 10, 1916.

Prof. C. VERNON BOYS, F.R.S., President, in the Chair.

A PAPER entitled "*Experiments Illustrating the Flow of Heat in Conducting Sheets*" was read by Mr. S. SKINNER, M.A.

If a sheet of tinned iron be heated locally by means of a Bunsen burner or blowpipe the tin is melted for a certain distance from the heated region. On allowing the sheet to cool the resolidified tin is separated from the unmelted tin by a very sharp line of demarcation. This line gives us the equi-temperature curve corresponding to the melting-point of tin. By pushing the heating to a greater or less extent a series of such equi-temperature curves can be obtained for a sheet of any particular shape heated at any given point. The cases shown illustrated the flow of heat into a rectangular plate from a heated tongue, into a circular disc from a heated tongue, round the corner of an L-shaped strip and into the vanes of an air-cooled

cylinder. The results were shown to be closely analogous to the flow of electricity in similarly shaped conductors.

DISCUSSION.

Dr. R. S. WILLOWS said a similar method had already been used by Voigt and his students to compare the thermal conductivities of different metals. They employed an organic substance which melted about 41° C. and gave a very sharp line on resolidification. Their method of heating was to place the metal strip on a red-hot copper block.

The PRESIDENT asked if the change of colour of mercuric iodide could not be used for this purpose.

Mr. EZER GRIFFITHS mentioned that if a sheet of steel be heated at the centre by means of a blowpipe, then on cooling a bright circular wave may be seen travelling towards the centre, due to recalescence. The converse effect was said to be observed during heating. The heat-indicating paints were the double iodides of copper-mercury (scarlet) and silver-mercury (yellow). Both darkened on heating, the former at 87° C. and the latter at 45° C., the change being reversible. They could be prepared by adding a solution of CuSO_4 or AgNO_3 to a solution of KI, redissolving the precipitate and adding a solution of HgCl_2 . Experiments involving the use of these paints are described in "Light, Visible and Invisible," by Prof. S. P. Thompson.

The AUTHOR said he was glad to hear about Voigt's experiments. He had seen the recalescence experiment mentioned by Mr. Griffiths. One trouble with paints used as heat indicators was that there was usually a considerable lag between the temperatures at which the change took place on heating and on cooling. Moreover, the line of demarcation was not very sharp.

A paper on "*The Absorption of Gases by Quartz Bulbs*," by Dr. R. S. WILLOWS, M.A., and H. TREVELYAN GEORGE, M.A., was read by the former.

The experiments are a continuation of those of Willows (*Phil. Mag.*, April, 1901) and Hill (*Phys. Soc.*, December, 1912) on the absorption of gas which is brought about by electrical discharges. A new quartz bulb does not absorb air, but if it be fed with repeated doses of hydrogen (which are absorbed when an electrodeless discharge is passed) it then becomes very active. If discharges in hydrogen are alternated with those in air the bulb can be made to absorb large quantities of either gas, and the activity with each gradually increases. The authors reject the theory of surface absorption, and, in their own experiments at least, also Swinton's theory that the gas is shot into the walls and held there. It is supposed that chemical actions occur with air and oxidation products are formed; these are reduced by hydrogen. The process is compared with the formation of the plates in a Planté cell, the absorption of hydrogen corresponding to the charging, and that of air to the discharging of the cell. Attempts to produce the same effects by chemical treatment are partially successful, particularly in fatiguing the bulb so that no further absorption takes place. The conditions under which the primary and secondary hydrogen spectra appear are also described.

DISCUSSION.

Mr. A. CAMPBELL SWINTON said he was very much interested in the subject. It was true that most of his experiments were done with tubes having electrodes, and there was very considerable heating. Under the bombardment of the cathode particles the inner surface of the glass may attain a very high temperature for a very short space of time. Sir J. J. Thomson had thought that it might almost become fluid and absorb the gas by ordinary diffusion. Sir J. Larmor, on the other hand, had conceived the molecules of gas to be hammered into the glass like tin-tacks by the cathode particles. Some of his experiments had been done with external electrodes of tinfoil tied round the outside of the tube. He had also obtained absorption of helium, which was not known to combine chemically with anything.

Dr. BRYAN described some experiments he had been making with a vacuum valve at pressures less than 1/1000th mm. Normally the electrodeless discharge will not work at this pressure, but it does so when a current is passed through the glower (tungsten filament). Under these circumstances the pressure rises, although after the valve has been running for some time the current in the filament when running by itself produces a decrease in pressure.

Dr. ECCLES, referring to the failure of gold leaf in certain circumstances to absorb mercury vapour, said that some workers were using silver for this purpose. It seems to have been used successfully for reducing mercury vapour pressure down to but not beyond a certain limiting vapour pressure.

Dr. H. S. ALLEN said that if a tube were coated with silver by spluttering from silver electrodes the layer so obtained was said to absorb mercury vapour very readily.

Dr. WILLOWS, in reply, said that Mr. Campbell Swinton's results with helium were not conclusive, as it was not certain that they were dealing with the same phenomenon. The discharge in a tube with external electrodes was not an electrodeless discharge at all. There was still cathode ray bombardment and strong local heating. It would be interesting to see if the experiments with helium could be repeated with a true electrodeless discharge free from any electrostatic effects. He thought Dr. Bryan's results could all be accounted for by gas coming out of the metal itself. He had not used silver to absorb mercury vapour because of the difficulty of getting it free from air. Mr. Harlow about two years since showed the Society an experiment similar to the one described by Dr. Bryan.

NOTICES OF BOOKS.

How the United States of America is dealing with the Shortage of Dye-stuffs. London: The Society of Chemical Industry. 1916.

THESE papers, which have been reprinted from the *Journal of the Society of Chemical Industry*, having been read at the meeting of the New York Section in October, 1915, contain many suggestions and hints which are worthy of the attention of British manufacturers and chemists. It was pointed out by the chairman of the meeting at which the papers were read that the manufacture of explosives is intimately connected with that of dye-stuffs, and that the very life of the nation is dependent upon the dyeing industry. The general question of the fostering of the American industry by the prevention of unfair foreign competition was the subject of a well-reasoned and forcible paper by Dr. E. E. Platt, and an interesting and illuminating account of the dye-stuff situation in the United States, by Dr. T. H. Norton, contained some references to the practical help given by Swiss chemists in solving the problem of the dearth of dyes in Russian textile works. Many suggestions are made in this paper as to the necessity for standardising dye-stuffs and their methods of application, and organising consumers, and the pamphlet as a whole deserves the careful consideration of all who are interested in the dye-stuff problem in this country.

Journal of the British Science Guild, January, 1916. London: 199, Piccadilly. Price 6d.

THE second number of the *Journal of the British Science Guild* contains articles dealing with organisation and education, and with the application of science to warfare. The report of the committee appointed to consider the question of the improvement of existing conditions governing the manufacture of microscopes in this country is also included. The report contains the suggestions of the committee as to the general types of microscopes which should be manufactured, and some notes relating to the reasons for the popularity of foreign instruments.

A Manual on Explosives. By ALBERT R. J. RAMSEY and H. CLAUDE WESTON. Pp. 116. London: George Routledge and Sons, Ltd. New York: E. P. Dutton and Co. 1916. Price 1s. net.

ANY attempt to popularise and spread scientific knowledge deserves support and encouragement, and this little manual seems likely to play some part in supplying information in a convenient form. It is intended principally for munition workers, whose interest in the question of the production of high explosives has been awakened, possibly for the first time, and it gives some brief explanation of the important part played by explosives in engineering problems. A short historical account is first given of the discovery of different explosives, beginning with gunpowder, and of the development of the modern industry. Then descriptions are given of the properties of explosives, and methods of making them most used nowadays are shortly described. The chapters on the application of explosives in peace as well as in war will be read with much interest, and the question of poisoning among explosive workers, its prevention and its treatment, is also very shortly discussed.

Proctor's Tables of Equivalents, Gauge Numbers, Inches Millimetres, Pounds, Kilogrammes, and Discount Book London: Edward Le Bas and Co., Dock House, Billite Street, E.C.

A NEAT little book for the pocket. The discount tables range from 1½ per cent to 98½, and the tables of metric weights with English equivalents and conversion factors are conveniently arranged for reference with a minimum of labour.

Although published at 1s. the firm have a limited number of copies that they are prepared to send by post at 6d. each, or 4s. per dozen.

CORRESPONDENCE.

INSTITUTE OF BIOLOGICAL STUDIES.

To the Editor of the *Chemical News*.

SIR,—I have the pleasure to inform you that the Constitutional Government has established a very important institution named Institute of Biological Studies, of the Secretary of Fomento, including the following departments:—I. The Institute of General and Medical Biology. II. The National Museum of Natural History. III. The Administrative Section. The departments of the Institute of Biological Studies are:—

I. *Institute of General and Medical Biology.*—1. General Biology. 2. Comparative Physiology. 3. General Biological Chemistry. 4. Industrial Biological Chemistry. 5. Medical Biology. 6. Marine Biology (at Veracruz). 7. Vegetal Biology. 8. Systematic Botanic and Mexican Flora.

II. *National Museum of Natural History.*—1. Mineralogy (Biological Mineralogy), Geology, and Paleontology. 2. General Systematic and Applied Botany. 3. General Systematic and Applied Zoology. 4. Biology. 5. Zoological Garden. 6. Botanical Garden. 7. Oceanographical Museum (at Veracruz).

III. *Administrative Section.*—The Director of Biological Studies, Prof. Alfonso L. Herrera. The Secretary, Dr. Leopo'do Flores. The Chief Librarian Clerk and Keeper of the Records, Prof. José L. Oteo. Three typewriters. Two guardians.

Buildings.—Institute of General and Medical Biology, 7th Balderas St., No. 94. National Museum of Natural History, 1st Chopo St.—I am, &c.,

A. L. HERRERA.

Mexico City, November, 1915.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—A degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 5, January 31, 1916.

This number contains no chemical matter.

No. 7, February 7, 1916.

Estimation of Reducing Substances in presence of an Excess of Saccharose. L. Maquenne.—The temperature has an enormous influence upon the reducing power of saccharose, and the author has confirmed M. Pellet's statement that the estimation should be carried out at temperatures below 100°, heating first to 85° and then keeping at 65° for ten minutes. Or a temperature of 62–64° may be maintained for twenty-two minutes. It is possible, however, to work at 100°, in boiling water for five minutes or boiling for three minutes, and this method presents certain advantages. The author recommends using 20 grms. of sugar when working at 65° and 10 grms. when using the method of boiling. Two methods can be used to determine the amount of copper reduced by a sugar. Either the precipitate can be collected and titrated by any exact method, or the copper remaining in the solution can be estimated. Both methods are excellent when the precipitate is abundant, but when the proportion of reducing substance is very small the first method must be rejected. Two principles can be based upon the author's investigations of the analyses of industrial sugars:—(i.). It is necessary always to work comparatively and in presence of a constant weight of saccharose. (ii.). The titration must be adapted to individual cases, reserving the usual methods based upon the separation of cuprous oxide to products rich in invert sugar and the hyposulphite method to those which are poor in it.

True Homologues of Glycerin: Heptanetriol.—J. L. Hammet.—The true homologues of glycerin have the general formula $\text{CH}_2\text{OH}(\text{CH}_2)_n\text{CHOH}(\text{CH}_2)_n\text{CH}_2\text{OH}$. The author has endeavoured without success to prepare the first homologue, pentanetriol, in which $n=1$, but he has obtained the second homologue, heptanetriol, by the following method:—The magnesium compound of 1,3-iodomethoxy-propane is treated with ethyl formate and then with water which gives the 1,7-dimethylol of 1,4,7-heptanetriol. This diether can be converted into glycerin by two methods, the most direct of which is treatment in the cold with two molecules of anhydrous hydriodic acid,—

$$\text{CH}_3\text{O}(\text{CH}_2)_3\text{CHOH}(\text{CH}_2)_3\text{OCH}_3 + 2\text{HI} =$$

$$= 2\text{CH}_3\text{I} + \text{CH}_2\text{OH}(\text{CH}_2)_2\text{CHOH}(\text{CH}_2)_2\text{CH}_2\text{OH}.$$

MISCELLANEOUS.

The International Correspondence Schools, Ltd., of Kingsway, London, have recently issued a series of pamphlets on the recapture and expansion of various British trades, that dealing with the chemical and allied trades having already been noticed in the *CHEMICAL NEWS*. In the others, which have for their subjects the electrical industry, mechanical engineering, the textile industries, &c., the causes of German supremacy are discussed, and some methods of combating German competition are suggested. The pamphlets contain matter of much interest to manufacturers and technical students, and the statistics given in them deserve the very careful consideration on the part of both commercial and scientific men.

Liebig's Extract of Meat Company, Limited.—The Directors have declared a half-year's dividend at the rate of 5 per cent per annum on the Preference Shares, payable, less Income Tax at 3s. 6d. in the £, on and after April 1 to the proprietors who are registered on the 20th inst. In respect of Coupon No. 31 of the Preference Share warrants to bearer, such dividend, less Income Tax at 3s. 6d. in the £, will be payable on and after April 1 at the Company's bankers, Messrs. Glyn, Mills, Currie, and Co., 67, Lombard Street, E.C.

International Scientific and Educational Amenities.—His Highness Raj Rana Sir Bawani Singh, of Jhalawar, Rajputana, who is much interested in educational matters, especially connected with Science teaching in India, writes as follows:—

"I have received with many thanks a copy of your most interesting Presidential Address at the Royal Society, and feel convinced that in your speech the British nation has got the soundest and most valuable advice which could be given at this critical period in her history. England has carried her conservatism too far; she has had the disposition to preserve all that was good in her, she has lamentably lagged behind in improving, and the result we find to-day is, to our great consternation, that Germany has stolen a march over us in the realm of science. Everybody will agree with you when you say that the English people will have to make many fundamental alterations in their ideas before they can become a Scientific Nation. India's future is indissolubly bound up with England's, and it will be of the greatest benefit to our country, as well as to the whole Empire, if your advice is immediately given effect to."

The following extract is taken from the *Mount Vernon Hawk-Eye* for January 20, 1916:—

"A personal testimony of the gloom and distress war creates was brought home to local circles this week in a communication from Sir William Crookes, the eminent English chemical authority, to Dr. Nicholas Knight, of Cornell College. A letter written from London and received this morning contains the following significant and impelling expression:—'Everything at this Christmas time here is very depressed, and the weather is gloomy and sunless. The cruel losses in the war are causing grief to most families, and the heavy taxation necessary is crippling the means of all families. If the murderous piracy on the high seas continues we are hoping that your powerful country will render us substantial assistance in putting a stop to it for the sake of humanity at large.'"

In a private letter to Sir W. Crookes, Professor N. Knight writes:—"I have forwarded a copy of your letter to President Wilson. I trust it will catch his attention and have weight in shaping the Nation's policy in respect to the German submarine warfare."

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Galathite.—Can any reader give name of British manufacturer of this substance?—G. S.

MEETINGS FOR THE WEEK.

- MONDAY, 27th.—Royal Society of Arts, 4.30. (Fothergill Lecture). "Surveying—Past and Present," by E. A. Reeves.
- TUESDAY, 28th.—Royal Institution, 3. "Modern Horticulture—Plants and the Seasons (Seasonal Rhythm)," by Prof. F. Keeble.
- Royal Society of Arts, 4.30. "Next Steps in Empire Partnership," by P. Hurd.
- WEDNESDAY, 29th.—Royal Society of Arts, 4.30. "Pan-German Aspirations in the Near East," by R. W. Seton-Watson.
- THURSDAY, 30th.—Royal Institution, 3. "English Music in the Tudor Period—Church Music," by Dr. W. H. Hadow.
- FRIDAY, 31st.—Royal Institution, 5.30. "The Spectra of Hydrogen and Helium," by Prof. A. Fowler.
- SATURDAY, April 1st.—Royal Institution, 3. "Radiations from Atoms and Electrons," by Sir J. J. Thomson.

THE CHEMICAL NEWS.

Vol. CXIII., No. 2940.

LOSSES AND OTHER CHEMICAL CHANGES IN BOILING VEGETABLES.

By KATHARINE I. WILLIAMS, M.Sc., The University, Bristol.

In a former article "On Cooked Food" in *Knowledge* (1912, xxxv.) the author gave some account of her investigations into the chemical composition of cooked fish and vegetable foods. It was fully explained that the main object of the investigations was to arrive at a clear idea of the value of food as served at table, and the results showed that many false ideas exist as to the proportion of nutrients contained; full details were given as to the preparation of the articles selected and the part played by water in the process of cooking, and attention was directed to the fact that the percentage of water is one of the most important parts of food analysis; we want to know how much solid food we really consume. In meat and fish there is a higher percentage of solid matter, and the whole of the flesh consists of nutrients, fat, protein, and mineral matter. Vegetables, on the other hand, besides these nutrients, contain starch enclosed in cell walls of fibre or, as it is also called, cellulose. The latter substance has a doubtful value from the food point of view as a nutrient. Inside this framework is found the starch; in the process of cooking the starch granules are gelatinised and break down the cell walls, as can be seen in a well cooked potato. The effect of cooking as regards solid matter is interesting, since after this operation the nutrients in the case of fish and meat show a higher percentage, whereas with vegetables the reverse is the case with a few exceptions. Only the edible portion is here considered—that is, the portion of vegetables that can be eaten as food. A simple definition of food is the one to be found in Dr. R. Hutchison's "Food and the Principles of Dietetics" . . . "anything which, when taken into the body, is capable of either repairing its waste or of furnishing it with material from which to produce heat or nervous and muscular work." The ordinary articles of diet are mixtures of various chemical substances, and among the most important of these are those containing nitrogen, examples of which are gluten in bread, legumin in pulses; but these are though different chemical substances and are classified under the general term protein. Non-nitrogenous is a term used for the carbohydrates, sugar, starch, also fats, such as butter. Another important group is called mineral matter (or ash), and here we have table-salt, also calcium specially found in asparagus and spinach, salts of iron also in spinach, peas, and potatoes; finally, water, which forms a large part of even our most solid looking foods. In this article it is proposed mainly to deal with vegetable foods. As a rule, most vegetables are sold in a vague way as to price—by the bunch with carrots; spinach, however, is sold by the pound. Three samples were bought about the same time at twopence each per pound:—(1). The waste was 4½ ozs. (2). Solid 1 lb. 3 ozs.; waste, 3 ozs. (3). The weight of the paper included was ¼ of an oz., 7 ozs. were waste (stems and roots), leaving only 8¾ ozs. for cooking purposes. The next question is how much refuse is there when bought? This consists of the skins of potatoes. Here, it may be remarked, care should be taken in the peeling of potatoes, as the layer next the skin is considerably richer in mineral matter and protein than any other part of the flesh; if this is wasted then the starch mainly forms the portion served at table. The best method to cook this vegetable is in the skin. With green peas the pods are often looked on as waste; they

form 45 per cent of the vegetable as sold, but can be used for soup provided some peas are added. A fact not generally known is that the pods are chopped up, boiled or steamed till the mass is soft; it is then crushed and passed through a sieve to separate the fibre from the edible portion; the latter is evaporated down, mixed with sugar, and sold as a kind of marmalade, or mixed with currants, gooseberries, or banana pulp and made into jam.

Refuse before Cooking.

(In 100 parts.)

Food.	Refuse.
Endive	52
Green peas	45
Parsnips	7½
Green artichokes.. .. .	72½
John Dory	21½
Cucumber	15
Borecole	38
Carrots	23
Celeriac	7
Vegetable marrow	18
Leeks	75
Gurnet	9

Two examples are given of the refuse in fish as sold, but it is often cleaned before leaving the shop, which is not usually the case with vegetables.

Before preparing the sample for cooking it was weighed, and then the refuse was weighed and percentage calculated; so now the remaining vegetable is weighed before and after the process of cooking, to determine the increase or decrease which is due to the loss or absorption of water. All waste is removed, such as the hard part of the stems of asparagus, bones and head of fish, shells of eggs. With one class of foods, the cereals, there is no refuse or waste; all is consumed as food.

Refuse as Served at Table.

(In 100 parts.)

Name.	Refuse.
Asparagus	34
New potatoes	2½
Green artichokes.. .. .	69
John Dory	21
Herrings	12
Haddock	35

All vegetables were simply boiled in water as supplied by the Bristol Water Company; this water is hard, due to the presence of calcium carbonate, but is otherwise excellent.

It will be seen some foods contain the two kinds of refuse, one the portion removed before cooking, the outer leaves of vegetables, the other the stems, bones of fish, &c., left after serving at table, and the asparagus is one example; this sample cost 9½d. per pound, only 31¼ per cent was fit for cooking, and of this 31¼ when cooked and served at table only 66 per cent could be eaten, making this vegetable an expensive article. A great deal of information has been published in America by the Department of Agriculture in "Bulletins" which are freely distributed in that country and can be bought by anyone for a few pence each; one in especial is valuable, No. 28 (Office of Experiment Stations), prepared by Prof. Atwater and A. P. Bryant, entitled "The Chemical Composition of American Food Materials"; it contains details of the analyses of 4065 American articles and commodities used for human food in that country, but in most cases they are uncooked.

We must now pass on to the main question—what are the principal changes that take place in the process of cooking? The first point is the change in the percentage of water; we could not live on dry foods—that is, foods

that contained no water; on the other hand, it is clear a high percentage results in a bulky food.

During the process of cooking meat and fish we have a decrease in weight. Prof. Grindley, of Illinois, has done a good deal of work on the subject of losses in the cooking of meat and the influence of cooking upon the nutritive value of meats. He found, besides losing water, some of the fat, protein, and mineral matters are dissolved out. He examined the extracts from boiling lean beef, and found as the average of 91 samples the loss of mineral matter was $44\frac{1}{2}$ per cent of the total amount present, of fat 12 per cent, and of protein $7\frac{1}{2}$ per cent. The same is true of fish. While nutrients are lost in the process, as is proved by the examination of the liquid after the meat is removed, a higher percentage of nutrients is found in the cooked condition and a lower percentage of water. With vegetable food the reverse is true; as commonly cooked almost all vegetables show an increase in the percentage of water and a lower percentage of nutrients. The question arises: Is this waste necessary; that is, can it be prevented? In *Bulletin* 43, Office American Experiment Stations, Prof. Snyder describes the loss in boiling potatoes, cabbage, and carrots. He found with potatoes the greatest loss was when they were peeled and soaked in cold water before boiling, amounting to one quarter of the total protein present—"in a bushel of potatoes the loss would be equivalent to a pound of sirloin steak." Less loss is sustained if the peeled vegetable is at once plunged into boiling water, as then the proteins are coagulated on the surface and make the inner juices less liable to loss. When the potatoes are cooked in their skins the best results are obtained. The loss of mineral matter by the first method is as high as 38 per cent. As generally cooked an excess of water has to be drained off; this is often thrown away. Prof. Snyder remarks with carrots a good deal depends upon the size of the pieces into which they are cut for cooking, the loss being greatest with small pieces. Often about 1 lb. of the sugar alone per bushel is removed, losing one-quarter of the total nutrients. To get the best food value the pieces should be large and the boiling rapid, and as little water as possible should be used. Cabbage in the raw condition only contains $7\frac{1}{2}$ lbs. of solid in 100 lbs., and of this $2\frac{1}{2}$ to 3 lbs. are lost in cooking. It is quite clear that such losses ought to be taken into account in drawing up dietaries. Further, such methods of cooking produce unpalatable dishes. Of losses found by the author in the course of her investigations spinach may be mentioned. In this case there are only 10 lbs. of solid in 100 lbs. of the vegetable; after cooking the loss is $2\frac{1}{2}$ lbs., about one-fourth of the total solid. Celeriac $9\frac{1}{2}$ lbs. of solid in 100 lbs. of raw, and the average of three samples shows $4\frac{1}{2}$ lbs. are lost. Curly greens or borecole 100 lbs. contain only 10 lbs. solid, and of this $5\frac{1}{2}$ lbs. are lost, in both cases about one-half of the solids. Turnips only contain about 9 lbs. of solid per 100 lbs., and here the loss is nearly 4 lbs. In cooking lettuce we find 1 lb. lost of the 4 lbs. (or one-fourth) solids in 100 lbs. of the raw vegetable. With the large variety of asparagus matters are rather better, as of the 8 lbs. solid only $\frac{1}{2}$ lb. is lost per 100 lbs. uncooked.

This, then, is the result of ordinary methods of cooking. Presumably the idea is that since vegetables are cheap it does not matter if nearly half their nutrients are thrown down the kitchen sink. Sir Henry Thompson, many years ago, drew attention to this waste in "Food and Feeding." The remedy he and others suggest is the use of the liquid in which vegetables are boiled for the foundation of soup, like the French peasant's "pot-au-feu." "To the pot of the peasant, who wastes nothing whatever, all things are welcome, and every atom of nutritive material—solid or liquid—goes into it, to which are always added herbs and vegetables, together with the liquor in which any of the latter may chance to have been boiled. Sometimes it is a pot maigre, no meat of any kind having been procurable, and very good vegetable soups, moreover, are educible therefrom."

Another method of cooking is coming to the front, and is called the "Conservative." Using this, vegetables are no longer merely washed-out stuff with all the goodness boiled and drained away and then pressed in a cloth. When the new method is employed as little water as possible is used, and that is absorbed or evaporates away. No draining or pressing is necessary, consequently there is no waste.

I have carried out some experiments recently to test the value of this process and found very satisfactory results. The first samples used were carrots and parsnips. In 1 lb. about one-twelfth of the total solid was lost, while more recently, with still more care in cooking green peas, celeriac, new potatoes, salsify, and turnips, the waste has been nil; all the water has been absorbed and the cooked vegetable has retained all its nutrients.

This series of vegetables was cooked in a Welbank's boilerette. These cookers are very simple in construction, and are practically a type of double saucepan. A certain amount of water is placed between the two vessels. The boilerette is then placed over the heating apparatus, and when steam comes through the valve the prepared vegetable can be put in the machine with half a tea-cupful of water. Some vegetables are better done when they are put into the basket which fits into the apparatus. Potatoes, for example, take rather longer cooking, but the process goes on by itself and does not need constant attention. Some cooks have used an ordinary saucepan for cooking spinach, with only the addition of just enough water to be absorbed, and in this method there was no loss of solids.

The two methods can be compared, and it is seen that to get the full value for the money spent the "Conservative" is the most economical. To return to the losses in cooking, it is interesting to know exactly which of the nutrients are lost and how the loss is ascertained. As soon as the process of cooking is finished the excess of water is drained off into an evaporating dish whose weight is known; heat is applied, and when only the solid is left the dish is again weighed and the percentage and weight of the loss is calculated. The solid is reduced to powder and analysed. The result of analysis shows none of the fibre, fat, or starch is lost, but carbohydrates in the form of sugar are, as has been said in the case of carrots, and is also true with beetroots. The most important losses are protein and mineral matter; with potatoes, protein 25 per cent, of the total mineral matter 38; carrots, loss of protein $6\frac{1}{2}$ per cent. Here the carbohydrate being mainly sugar the loss is 25 per cent of mineral matters, 37 of the total present in each case.

The percentage per 1 lb. of the following vegetables shows the loss in the total solids:—Celeriac, loss one-half, of this 7 per cent was mineral matter and 54 per cent protein; curly greens, two-fifths of the total solid, $15\frac{1}{3}$ of this is mineral matter, 41 per cent protein. Chicory, one-fifth of solid lost; of this $42\frac{1}{2}$ per cent protein, 12 per cent ash. Butter-beans lost one-tenth of the solids, of which 28 per cent was protein, $5\frac{1}{2}$ per cent ash. Endive, total loss about one-fourth of the solid; of this 29 per cent was protein, 18 per cent ash. These mineral matters are needed by the human body as tissue formers, and can supply the potassium, calcium, iron, phosphorus, and sulphur in an ordinary diet; calcium and phosphorus in milk, the latter also in carrots, turnips, potatoes, various varieties of beans and peas. Iron among other sources is found in the yolks of eggs, oatmeal, potatoes, spinach, and apples. Prof. Sherman, of the University of Columbia, in *Bulletin* 185, Office Experiment Stations, gives details as to the value of iron in food and the needs of the human body. He also goes into the question of calcium, magnesium, and phosphorus. In *Bulletin* 227 he, with the assistance of others, gives full details of their dietary studies, the desire being to solve the question, how much of these elements are needed in the human diet?

The next important question is as to the percentage of water. When cooked in an excess of water which is drained off, the cooked article contains more water than

the uncooked. Cooked the Conservative way in the boilerette the percentage sometimes varies, in the other method a lower percentage in the cooked vegetable is quite an exception.

The Percentage of Water in the Raw and Cooked Conditions.

Name.	Raw.	Cooked.	Cooked in boilerette.
Scarlet runners ..	93	94	—
Beetroot	82	83	—
Endive	91	95	—
Parsnips	76	81	79
Green peas	70	87	73
Celeriac	91	94	89
Jerusalem artichokes	80	92	79
New potatoes	81	—	83
Salsify	82½	84	80

Two vegetables on this list are not as well known as they ought to be, the names are even unknown by green-grocers doing a fairly good business; salsify is one of them. The roots can be left in the ground until late in the season, and it comes into use as a variety in the winter. It is often called the oyster plant, because the flavour suggests that of oysters. The other vegetable is celeriac, which is also known as "knot celery" and "turnip rooted celery"; the roots only are eaten. It also comes into the market during the winter. Its flavour is something like celery.

In another class of vegetable foods the change in the percentage of water is still more marked; that is the pulses. In dealing with these foods one of the most important factors to consider is the amount of protein present. We often see the statement that the pulses are rich in this nutrient, and for this reason they are called "poor man's beef." This is true only in the uncooked condition, but not as we eat them. This idea arises from the incorrect method of describing the results of analysis. In most tables the percentage of water is left out, and only those of fat, fibre, protein, and carbohydrates are given, thus making these percentages appear higher than they really are; also the comparison is between meat and pulses in the uncooked state. Here we find for protein, beef 22, veal 20, mutton 20, lentils 22, peas (dried) 21. Now, in the process of cooking, meat has lost water; therefore the percentages of fat and protein are higher in the cooked condition, while with the pulses the reverse is the case, so that all the percentages of the nutrients are lower:—Beef (boiled), 34; veal (roasted), 29; lentils, 9; peas, 9; that is, the percentage of protein in the natural moist condition as served at table.

Percentage of Water.

Name.	Uncooked.	Cooked.
Beef	71	57
Veal	71½	58
Mutton	67	51
Lentils	12	66
Peas (dried)	14	62

With cereals, such as oatmeal, we have no loss of nutrients; all the water used in cooking is absorbed. Starting with 10 lbs. of each of the following articles we find provost barley and oats 60½, frame-food 156, plasmon arrowroot 113, rice (prepared by a Conservative method) 36 lbs.

These, then, are the chief changes in cooking vegetable foods, and it cannot be satisfactory that so much of the valuable nutrients should be lost by bad methods of preparation. It may be said vegetables are cheap, but the great object of cooking is to make food attractive and wholesome, and it is the salts which give the flavour. It is a pity the subject of the scientific value of food is not studied in this country in the same way that it is in America. Much can be learnt from the publications of the Department of Agriculture in that country.

THE INFLUENCE OF COMPOSITION UPON THE CORROSION OF STEEL.*

By LESLIE AITCHISON, M.Met.

(Concluded from p. 137).

Manner of Experiments and Results Obtained (continued).

THE structurally free carbides in the series show the greatest possible regularity. Throughout the list of steels under review each carbide acts in the same way, being entirely unattacked. Whenever these carbides stand by themselves, whether as crystal boundaries and globules as the result of segregation or in relatively large masses, the result is the same—they remain quite unattacked. This may be seen very well in Figs. 8 and 9 (*supra*) as illustrating the case of crystal boundaries, in Fig. 10 (No. 37, having 12.45 per cent of vanadium), in Fig. 4 (*supra*) for the isolated globules, and in Fig. 11 (No. 46, having 5.37 per cent of tungsten) for the large masses. The case of the segregated carbides is seen very well in the nickel steels, particularly Nos. 55 and 56, for there the pearlite and ferrite are corroded distinctly, but where there has been a separation of the pearlite into ferrite and cementite the latter is quite unattacked. Also in Fig. 12 (No. 33, with 0.6 per cent carbon and 0.71 per cent vanadium) a certain amount of segregation has taken place, the result being that the carbide boundaries stand out alone and unattacked.

The solid solution which occurs in most of the alloy steels is also quite uniform in its behaviour. In general it is attacked fairly evenly, leaving the free carbide which accompanies it, and which may be safely assumed to act as its electrical cathode, standing up quite alone and unattacked. The even attack is seen very well in Fig. 13 (No. 47, having 0.74 per cent of carbon and 14.96 per cent of tungsten), and the more uneven, due to the extra carbide dotted about in the solid solution, in Fig. 14 (No. 44, having 0.73 per cent of carbon and 21.5 per cent of tungsten). These two structures are quite typical of the steels containing solid solution and free carbides.

The influence of the inter-granular material referred to above is seen in several of the samples. The effect of the corrosion upon it is evident in Fig. 4. There may be noticed here relatively broad black lines surrounding the grains. These are not optical effects at all, and in the actual specimen show up quite plainly and quite definitely. It seems fairly certain that this layer of material has been attacked preferentially at the commencement of the corrosion, or perhaps has been the centre of the action between the two adjacent crystals. Whatever the action may have been it has resulted in the production of a narrow pit, the sides of which have been exposed. These sides are relatively rough, and consequently offer a fairly large surface to the attack of the solution. In consequence there has been a relatively intense action in these regions. This would account for the slightly greater attack on the bar iron over that sustained by the steels with a higher carbon content. The inter-granular layer naturally does not appear in those steels having carbide boundaries to the crystals, but does appear in some of those steels having solid solution with very little free carbide, and that as globules scattered about within the grains (*cf.* No. 45, with 0.70 per cent of carbon and 9.74 per cent of tungsten, also in several of the chromium steels). The steel examined for the action of twinning was corroded in the same manner as the other steels, but it was found that the corrosion had gone on to a very great extent, the structure being entirely obliterated. (This is not due to the twinning alone, as a nickel steel possessing an almost identical structure did not corrode at all). By corroding for a shorter period (three days) the structure shown in Fig. 15 was obtained. This shows that the parts of every steel orientated in different ways, corroded

* A Contribution to a General Discussion on "The Corrosion of Metals" before the Faraday Society, December 8, 1915.

to different extents, though neither was quite free from attack. Evidently the existence of twinning is likely to hasten the corrosion of any material showing a tendency to be attacked.

The microscopic results, coupled with the results obtained by the attack by the various corrosive media, tend to prove the following interesting conclusions:—

the true homogeneity that might be expected to furnish a resistance to corrosion, since they may possess twinned crystals, which certainly aid corrosion, or may be in a state of thermal or mechanical strain.

2. That non-homogeneity is not in itself productive of a more easily corrodible steel. This is seen very well in the case of the chromium steel (No. 27, containing 19.46 per

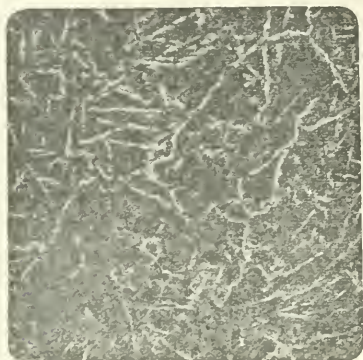


FIG. 8.—C 1.25.

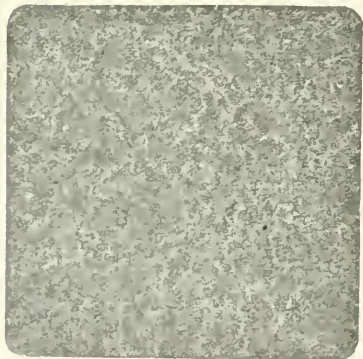


FIG. 9.—C 1.30, V 0.21.

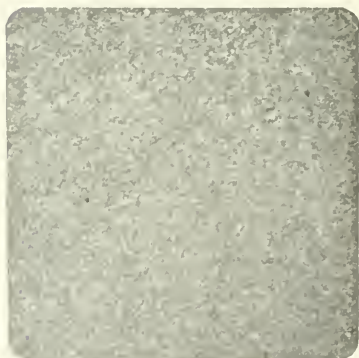


FIG. 10.—C 1.10, V 13.45.

1. That in ordinary metallurgical experience no steel is sufficiently homogeneous to be able to resist corrosive attacks. The most homogeneous material is the bar iron (No. 1), and yet this contains in itself the elements of a non-homogeneity (the amorphous inter-granular cement) which is sufficient to give it a very considerable corrodibility. Also that steels chemically homogeneous have not

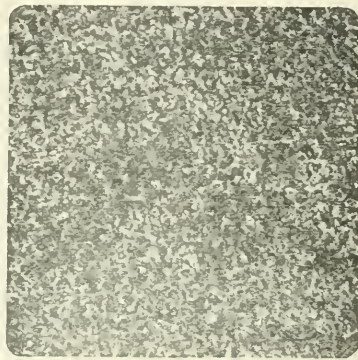


FIG. 11.—C 0.72, W 5.37.

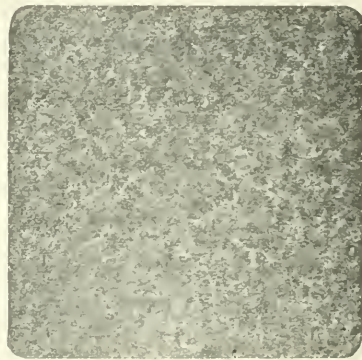


FIG. 12.—C 0.60, V 0.71.

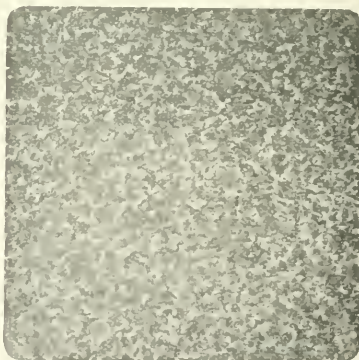


FIG. 13.—C 0.74, W 14.96.

cent of chromium), which is not corroded at all in the 3 per cent sodium chloride solution, but which has a structure essentially non-homogeneous (composed of carbides and solid solution mixed together most intimately).

3. That the true secret of non-corrodibility lies in some property of the solid solution—probably its solution pressure as reflected in its contact potential against the

solution—which is to be found as a consequence of the chemical composition only, coupled with the thermal and mechanical treatment. Apparently iron itself is not capable of offering real resistance to corrosion because its solution pressure is never sufficiently low. It is hoped that the results of work in support of this view may be communicated shortly.

4. That carbides in steels act in two directions—(a) as deterrents, in that they resist corrosion in themselves, being quite unattacked by the majority of reagents; (b) as aids in most cases, by providing a suitable cathode to act as counter to the anodic action of the ferrite in solid solution. In this latter way the presence of pearlite, which of course contains the carbide in considerable quantities, tends to increase the corrodibility of the steels. Although the pearlite appears in most cases to be attacked, it is most probable, in view of the persistence of the free carbides, that the attack is confined to the ferrite or solid solution. This latter of course constitutes the matrix in which the small rods or lenticles of carbide are embedded, and the disappearance of this support results in the mechanical removal of the carbide and not in the solution or decomposition of it. This is supported by the fact that in every case of a metal containing any quantity of carbide (either

THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES.*

By ROGER C. WELLS.

(Continued from p. 139).

FRACTIONAL PRECIPITATION.

Previous Investigations.

Most of the separations made in analytical chemistry depend on pronounced differences in solubility and the use of an excess of reagent, but in geochemistry we have to consider associated substances whose solubility may differ but slightly and whose formation was due to fractional precipitation. A fractional precipitation is one in which only a part of the dissolved substances pass from solution to solid.

The theoretic side of fractional precipitation was treated extensively by Berthollet over a century ago. As regards fractional precipitation Berthollet was correct in contending that the composition of the precipitate might be indefinite, and Prout's view as to the definite composition of the precipitate was correct in regard to pure simple

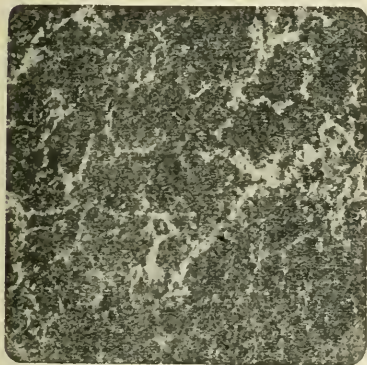


FIG. 14.—C 0.73, W 21.5.

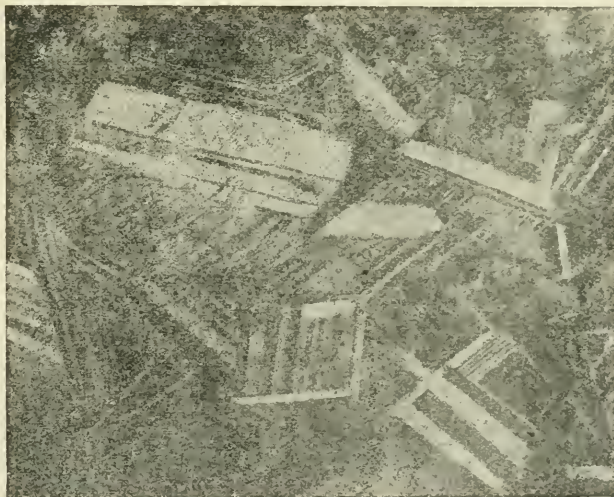


FIG. 15.—C 1.2 per cent, Mn 12.0 per cent.

ree or in the pearlite) the sample after corrosion was covered with a loose layer of carbide that had to be removed before weighing. In the case of those pieces of carbide that are relatively large it is quite conceivable that they are rooted so deeply in the ferrite or solid solution that the corrosion has not proceeded to the depth required to cause them to be loosened sufficiently to be removed by mechanical means. Similarly of course the boundaries of the grains are firmly fixed in the material and are not likely to be removed.

Action of Mercury Salts on Aluminium Foil.—St. Minovici and Em. Grozea.—When some drops of a solution of corrosive sublimate are placed on aluminium foil and allowed to dry they leave an efflorescent residue like that of calcium nitrate which forms on damp walls. This reaction occurs very rapidly, and is very sensitive. No other salt prevents its occurrence, but it does not take place if the aluminium foil with the mercury salt is heated in a flame, nor is it produced *in vacuo*. All salts of mercury give it, and it appears probable that it might be used in general analysis and in toxicological researches.—*Bulletin de la Section Scientifique de l'Académie Roumaine*, [6], iv., 227.

chemical compounds. Berthollet held that the fundamental factors in chemical reactions are cohesion, elasticity, and mass relations, governing respectively solubility, volatility, and precipitation.

Fractional precipitation of the rare earths has long been familiar to chemists. In this way the constituents of the gadolinite earths were separated by Mosander ("On Yttria, Terbium, and Erbium," *Phil. Mag.*, 1843, 3rd ser., xxiii., 252), praseodymium and neodymium were separated from the cerite earths by Welsbach, the constituents of the yttria earths were separated by Crookes ("On the Methods of Chemical Fractionation," *CHEMICAL NEWS*, 1886, liv., 131, 155), and the sulphide of polonium by Curie ("Radio-active Substances," *CHEMICAL NEWS*, 1903, lxxxviii., 146). Debus, in 1853, made quantitative experiments on the fractional precipitations of barium and calcium carbonate ("Ueber Chemische Verwandtschaft," *Liebig's Ann.*, 1853, lxxxv., 124), and Chizynski later studied the phosphates of these two metals ("Ueber die Chemische Massenwirkung," *Ann. Chem. Pharm.*, 1865, Suppl. Bd. 4, p. 226). Chroustchoff and Martinoff studied the precipitation of sulphates and chromates by a barium salt

* *Bulletin* 609, United States Geological Survey.

"Des Coefficients d'Affinité Chimique," *Comptes Rendus*, 1887, civ., 571, and Küster and Thiel the fractionation of bromides and thiocyanates by silver nitrate ("Ueber Gleichgewichtserscheinungen bei Fällungsreaktionen," *Zeit. Anorg. Chem.*, 1902, xxxiii., 129). Recently Goldblum and Stoffella have studied the system involving lead carbonate and chromate ("Contribution à l'étude de l'Affinité Chimique," *Journ. Chim. Phys.*, 1910, viii., 135).

The advantage of studying fractional precipitation for a theory of ore deposits is that the results show the net effect of all the factors that enter into play, including even unsuspected factors. Thus, if the salt of one metal is more hydrolysed in solution than another, or if a metal has a tendency to form basic salts, the effect will be manifest in the fractionation.

An objection that may be made to many laboratory experiments is that chemical precipitates are formed instead of natural minerals. For some purposes this objection is valid; for others not. In general, such experiments will shed light on the relations to be expected in the formation of minerals. In fact, in many experiments it has been shown that in the course of a few hours the precipitate alters even at ordinary temperature into the mineral, as does lead sulphide (O. Weigel, "Die Löslichkeit von Schwermetallsulfiden in Reinem Wasser," *Zeit. Phys. Chim.*, 1907, lviii., 293). In other experiments the rate of alteration is very slow, as Allen and Crenshaw have shown for zinc sulphide ("The Sulphides of Zinc, Cadmium, and Mercury," *Am. Journ. Sci.*, 1912, 4th ser., xxxiv., 358), and solubility determinations are needed for the minerals as well as for the amorphous precipitates. I have, however, found in every experiment in which the effect of time has been noted, that when equivalent quantities of two metallic salts are taken the experiment shows almost at once which of the two metals forms the more insoluble compound. There may be a decrease in solubility with time or a relative change in the solubilities on account of the very gradual development of the most stable compounds, but in no experiment did the metal first precipitated in excess later become the more soluble.

Method of Experimentation.

The metallic compounds will be discussed in the order of their solubility—sulphides, hydroxides and oxides, carbonates, bicarbonates, and silicates.

The procedure in the experiments on fractional precipitation was simple. A dilute solution containing two metallic salts in equivalent quantities was precipitated by reagent enough for one metal only. After a time an aliquot part of the mother-liquor was analysed, and the composition of the precipitate was determined by difference. In some experiments the proportions were varied slightly, as noted.

Table for Computing "Equivalents."

For weight given of	Divide by	For weight given of	Divide by
Ag	107.87	Mg	72.16
Al	9.033	Mn	27.46
Ba	68.68	Na	23.00
Cd	56.20	Ni	29.34
Ca	20.03	Pb	103.50
Co	29.48	Zn	32.68
Cu	31.78	Cl	35.45
Fe'	27.92	CO ₃ '	30.00
Fe'''	18.61	HCO ₃ '	61.01
H	1.008	NO ₃	62.01
Hg'	200.6	SO ₄ '	48.04
K	39.09	HSO ₄ '	97.08

Since the quantities of salts used are frequently expressed in equivalents a table has been prepared to assist in making conversions from units of weight to "equivalents." An equivalent is the molecular weight of a radicle (or atomic weight of an element that constitutes a radicle) reduced to a univalent basis. The equivalents

thus calculated correspond to the usual chemical equivalents of salt radicles in aqueous solutions referred to eight parts of oxygen. Of course, equivalent weights of salts may be taken in mgrms., grms., pounds, or tons, but wherever no qualification is expressed grm. equivalents are always understood.

SULPHIDES.

Solubility of Sulphides.

As these experiments were made to determine the order of solubility of the compounds studied, it will be advantageous to present first such data as already exist on the subject.

The sulphides of the heavy metals are very insoluble. Although they are ordinarily considered quite insoluble their solubilities can be determined approximately by physico-chemical methods, and, in fact, it has been shown that mercuric sulphide is many thousandfold more insoluble than manganous sulphide. The solubility of the sulphides in water at 18° C. was determined by Weigel by the conductivity method ("Die Löslichkeit von Schwermetallsulfiden in Reinem Wasser," *Zeit. Phys. Chem.*, 1907, lviii., 293), but the determination of the solubility by this method is complicated by the fact that the exact nature of the dissolved substances must be known, and as the sulphides produce solutions differing in alkalinity the method could hardly be expected to yield more than mere approximations to the true solubility.

Solubility of the Sulphides of the Heavy Metals in Distilled Water at 18° C. according to Weigel.

(Mols. $\times 10^{-6}$ per litre).

Crystallised sulphides.

SnS	0.14
As ₂ S	0.55
SnS ₂	1.13
Galena (from precipitated PbS)	1.18
Galena (Freiberg)	1.21
Cu ₂ S	3.1
Zinc blende (artificial)	6.63
Zinc blende (Santander)	6.55
Greenockite (artificial)	8.99
Millerite (artificial)	16.29
Wurtzite (artificial)	28.82
Pyrite (artificial)	40.84
Pyrite (Freiberg)	48.89
Pvrrhotite	53.6
MnS	54.5

Freshly precipitated (probably amorphous) sulphides.

HgS	0.05
Bi ₂ S ₃	0.35
Ag ₂ S	0.55
As ₂ S ₃	2.1
CuS	3.51
PbS	3.6
Sb ₂ S ₃	5.2
CdS	9.00
NiS	39.87
CoS	41.62
FeS	70.1
ZnS	70.6
MnS	71.6

The solubility products of sulphides have been determined by other investigators from time to time.

(I. Bernfeld, "Studien über Schwefelmetallelektroden," *Zeit. Phys. Chem.*, 1898, xxv., 46; Joseph Knox, "A Study of the Sulphur Anion and of Complex Sulphur Anions," *Faraday Soc. Trans.*, 1908, iv., 48; C. Immerwahr, "Beiträge zur Kenntnis der Löslichkeit von Schwermetallniederschlägen auf Elektrochemischen Wege," *Zeit. Elektrochem.*, 1901, vii., 478; S. Glixelli, "Zur Theorie der H₂S Fällung der Metalle—Die Einwirkungen von Schwefelwasserstoff auf Zinksalze," *Zeit. Anorg. Chem.*, 1907, lv., 306; R. Lucas, "Gleichgewichte Zwischen Silbersalzen," *Zeit. Anorg. Chem.*, 1904, xli., 211; L. Bruner and J. Zawadzki, "Ueber die Gleichgewichte bei der Schwefelwasserstofffällung der Metalle," *Zeit. Anorg. Chem.*, 1910, lxx., 136).

For a univalent, bivalent, and trivalent metal, respectively, the solubility products (S.P.) would be:—

$$\begin{aligned} \text{S.P.} &= [\text{M}^+]^2 [\text{S}^-] \\ \text{S.P.} &= [\text{M}^{++}] [\text{S}^{--}] \\ \text{S.P.} &= [\text{M}^{+++}]^2 [\text{S}^{---}]^3 \end{aligned}$$

The values of the solubility products already published were collected by Bruner and Zawadzki, who also calculated them from the heat of formation of the sulphide,

and the electrolytic potential of the metals and of sulphur. In the table below I have placed their calculated values of the solubility products, those found by the observer noted, and finally the "solubility of the sulphide in water" calculated from the solubility product. It will be noted that the solubilities in this table are far smaller than those obtained by Weigel.

Solubility Products of several Sulphides and their Solubility in Water.

(Based on determined solubility product, if known; otherwise on solubility product calculated by Bruner and Zawadski).

Sulphide.	Solubility product calculated.	Solubility product found.	Solubility in water. Mols. per litre (calculated).
*MnS ..	7.0×10^{-16}	—	2.6×10^{-8}
*Ti ₂ S ..	(4.5×10^{-23})	(4.5×10^{-23})	2.2×10^{-8}
*FeS ..	7.0×10^{-22}	3.7×10^{-12}	1.9×10^{-11}
†BZnS ..	6.0×10^{-24}	1.1×10^{-24}	1.0×10^{-12}
†aZnS ..	—	5.0×10^{-26}	2.2×10^{-12}
*NiS ..	7.0×10^{-25}	—	8.4×10^{-13}
*CoS ..	1.5×10^{-26}	—	1.2×10^{-13}
*PbS ..	2.1×10^{-28}	3.4×10^{-28}	1.8×10^{-14}
*CdS ..	1.8×10^{-29}	5.0×10^{-29}	4.2×10^{-15}
†Ag ₂ S ..	1.4×10^{-48}	4.8×10^{-53}	2.3×10^{-18}
‡Ag ₂ S ..		1.5×10^{-50}	1.9×10^{-17}
Ag ₂ S ..		3.9×10^{-50}	2.2×10^{-17}
*CuS ..	7.0×10^{-45}	5.9×10^{-42}	2.4×10^{-21}
CuS ..		1.2×10^{-42}	1.1×10^{-21}
HgS ..		2.8×10^{-54}	1.7×10^{-27}
*HgS ..	1.0×10^{-49}	6.7×10^{-48}	2.4×10^{-24}

* Bruner and Zawadski.

† Glixelii.

‡ Lucas.

§ Bernfeld.

|| Knox.

* Immerwahr.

** Based on different heats of formation.

The order of solubility obtained from experiments on fractional precipitation should agree with the order of solubility given in the last column of the table. As a matter of fact, the agreement is excellent except for two metals, silver and cobalt. The discrepancy for silver requires explanation; that for cobalt is not surprising in view of the small difference between its solubility and those of the adjacent sulphides. The discrepancy for silver may be due to a failure of the principle of the solubility product, as silver sulphide is a univalent compound, or possibly to the precipitation of silver by sulphides in part as free metal. A study of the fractional precipitation of thallous sulphide would assist in deciding between these two possibilities. Weigel's series seems to place silver in its proper position, but it shows several discrepancies for other metals.

While the solubility of sulphides is under consideration attention may be paid briefly to the enormous effect of changes in acidity on the precipitation of sulphides. This effect is due to the nature of the ionisation of hydrogen sulphide, the sulphide ion concentration varying inversely as the square of the hydrogen ion concentration for a given concentration of total sulphide. As is well known, the precipitability of the sulphides varies so greatly that a complete separation of certain groups is possible. Thus in an acid solution hydrogen sulphide added to a dilute mixture of the sulphates of iron and copper precipitates almost wholly copper sulphide. This is not strictly a fractional precipitation, since in an acid solution of hydrogen sulphide the concentration of sulphide is probably not sufficient to exceed the solubility product of ferrous sulphide. A fractional precipitation would be obtained with a small amount of precipitant under conditions which would permit all the metals to be precipitated with an excess. With iron and copper sulphates, for example, a fractionation might be made with sodium sulphide, since an excess of sodium sulphide would precipitate both sulphides completely.

Experiments with the Nitrates of Copper and Lead.

The first experiments on this point showed that the composition of the precipitate depends a great deal on the manner of precipitation and time of standing. A mixture of the nitrates of lead and copper, partly precipitated with a solution of hydrogen sulphide in the cold and filtered within a short time, yielded a precipitate containing the sulphides of both metals, although copper was slightly in excess. On warming, however, copper sulphide was the chief product, being precipitated even at the expense of the lead sulphide first formed.

(To be continued).

THE REFORM OF THE MAN OF SCIENCE.

SOME correspondence has recently appeared in the *Morning Post* under the title that stands at the head of this article. Lieut.-Colonel J. W. Barret, of the Australian Army, a Melbourne doctor, well known for his active participation in the educational world there, writing respectfully of British men of science laments their exclusiveness. They are, he implies, too much dominated by the idea of studentship; they regard the sphere of science too much as that of the laboratory and the academy; they do not acknowledge brotherhood with men in the greater world, who, in the spirit of enterprise and with the kind of method that prevail in conventional science, are solving great problems of industry, commerce, and national development. Another writer goes further, and would hail as a brother in science the man who elucidates the authorship of Shakespeare's plays or the technique of an old master.

It is not proposed here to enter upon a discussion of the legitimate use of the term science. We may be all for brotherhood, but the circumstances of life compel us largely to separate into groups for purposes of action, and there can be no real complaint if the word science is used in a restricted sense for what is perhaps better called natural science. This should not prevent men of science from recognising their kinship with all faithful workers for the elucidation of truth in whatever sphere of action.

Let us avoid a controversy about mere words. Lieut.-Colonel Barret's complaint is a more substantial one—not one of terminology. It is essentially this, that when operations relating to the forces of nature transcend a certain scale they are no longer recognised as science, and that men of science in the limited sense thus lose a great companionship and an invaluable link with the greater world. He gives as an illustration the work of a railroad president whose operations "involve the placing of towns and even cities in new positions, the reorganisation of the agricultural education of districts, the estimation of future markets, and other complicated actions involving scientific imagination of the first order."

It is probable that most men of science would readily admit that some solid advantages would be gained by having in their camp these great operators, with all their intellectual energy, their enterprise, and their influence, and perhaps many would admit their claim to inclusion. There is undoubtedly a tendency for an increased scale of operations to remove a man from the scientific class if he was once in it, or to prevent his accession if he did not originally enter through the usual portal. The case may be well illustrated from engineering. A scientifically trained engineer who betakes himself to great problems of engineering, constructing some almost impossible railway or irrigating a whole parched province of India, seems to be moving away from science. An engineer who has acquired such powers without having received the hallmark of formal scientific training will find it hard to get his place acknowledged in the ranks of science.

We may ask, What is really at the bottom of this? Is it merely narrow-mindedness, or is there something more

excusable? It is pleasant to think that there may be. Scientific men in their most august society are banded together "for the improvement of natural knowledge." They are by implication a body of students working in the temple of nature for truth's sake alone, heedless of the world and its rewards. What they garner is their gift to the world; they fill another page in the revelation that brings men nearer to the angels. Let a man wander into the world with his science as wares to sell for money profit and he has passed from the true brotherhood. Surely this idea, perhaps here rather fancifully stated, is at the bottom of much of our exclusiveness. It is certainly expressed very often in the privacy of small deliberative councils and in personal intercourse, and it is strongly, though silently, operative in the outer world.

If this were the chief reason for the detachment of men of science we should have to ask whether it be really good and sufficient. That it has elements of good in it no one would deny. There should be much strength in the union of disinterested people, and the flame of disinterested—that is, unworldly—study is the most sacred light of knowledge. But there is this great fact of history and actuality against an austere brotherhood: natural science has had its roots in the practical avocations of mankind, and from them it has received its chief stimulus. The application of science to the practical arts has not more benefitted them than it has benefitted science. In this place it is unnecessary to illustrate or amplify the argument. It is therefore not only not unbecoming, but it is vitally necessary that the improvement of natural knowledge should be bound up with solving the problems of the busy world, and the man of science who looks with any kind of disdain on those who are engaged in solving these problems—be they labelled brewer, baker, or candle-stick maker, and be they incidentally making fortunes—is despising his best friends and declaring himself a pedant.

As a matter of fact this disdain does linger. It is the inevitable product of the seminary, it is the fatuity of the cloister, arising no doubt from the theological beginnings of our educational system—this notion of keeping science unspotted from the world. It has much to answer for. The neglect of applied science—what is it not meaning now in the fortunes of our nation! It is comfortable for us to blame anyone but ourselves. Have we not long proclaimed the vital importance of science for the service of industry and the State? Industry and the State are doubtless much to blame, but surely no fair-minded person would say that the scientific world is exempt. Rather let us acknowledge that Lieut.-Colonel Barret is in essence right. The scientific world has been too exclusive; it has not bound itself as much as it might have done to great workers in the world, whose tasks, if not the same, are much akin to those of the laboratory; men whose sympathies, already scientific, would be strengthened by association, and make broad channels for the flow of science into practice.

Scientific men, we must admit, have often no conception of the real environment and problems of the industrialist, of the accumulated store of empirical knowledge from which he must select what is needed, of the skill and design with which he must apply it under the limitations imposed by men, material, and markets. They too often underrate the extent and importance of what may be called technological science and the new horizon that it opens. The technologist is often ignorantly set in the outer courts of learning; he is not quite of the elect, and antipathies arise. How much have we not sacrificed of the acceptance and efficacy of science in industry by offering young men trained in pure science and knowing nothing of manufacture to employers trained in manufacture and knowing nothing of science, relying wholly on the manufacturer for a most difficult and precarious adjustment?

The management of our applied science has become one of the great problems of the day, and it brings with it great difficulties. Spurious technology is a hateful make-

believe that has already wrought much mischief; a man, however scientific, wholly on the make—to use a concise vulgar term for a vulgar condition—is an unedifying spectacle; but it does not follow that because a man is preoccupied with industrial problems he shall lose his scientific virtue, or that his achievements, however remunerative, should rank on a lower plane. It is not so difficult to distinguish the genuine from the base among scientific workers wherever they may be engaged.

We must strengthen the bonds between science and industry by something more than an appeal to the pocket. A real sympathy and interest must be created on both sides; we must open our arms wider. Even if we find difficulty in discovering in this country the type of railway president described by Lieut.-Colonel Barret, there are yet many men in our world of industry and in the service of the State who, without any list of scientific memoirs to their name, have yet been potent in the service of science and would be more potent still if they were brought more into companionship with the scientific world. The Royal Society has the power of admitting to its ranks at the rate of one each year "persons who in their opinion have either rendered conspicuous service to the cause of science or are such that their election would be of signal benefit to the Society." Here at least is a limited opportunity of doing something towards introducing into the circle of science the sort of men whose influence might help towards bringing about the reform to which we are bidden by a candid friend. In any of the new associations that are contemplated for giving science its right place in our national life we shall surely do well to cast our net widely and to extend our outlook beyond the conventional circumference of what have usually been deemed scientific circles.—*Nature*, March 16, 1916.

THE ROYAL SOCIETY.

ORGANISATION OF SCIENTIFIC EFFORT.

A CONFERENCE convened by the President and Council of the Royal Society was held at Burlington House on Wednesday, the 22nd inst., to consider the desirability of establishing a Conjoint Board of Scientific Societies for the purpose of organising scientific effort in this country. Delegates from the following societies attended to confer with the President and Council of the Royal Society:—

The Royal Society of Edinburgh.
The Royal Society of Arts.
The Royal Anthropological Institute.
The Royal Astronomical Society.
The Royal College of Physicians.
The Royal College of Surgeons.
The Royal Geographical Society.
The Royal Institution.
The Institution of Civil Engineers.
The Institution of Electrical Engineers.
The Institution of Mechanical Engineers.
The Institution of Mining Engineers.
The Institution of Naval Architects.
The Institute of Chemistry.
The Society of Chemical Industry.
The British Association.
The Chemical Society.
The Geological Society.
The Linnean Society.
The London Mathematical Society.
The Physical Society.
The Physiological Society.
The Zoological Society.

The following resolution was passed unanimously and a Committee was appointed to draft a scheme for giving effect to the resolution, and to report thereon to a future meeting, viz:—

This meeting considers that it is desirable to establish a Conjoint Board of Scientific Societies for the purpose of—

- (1) Promoting the co-operation of those interested in pure or applied science;
- (2) Supplying a means by which the scientific opinion of the country may, on matters relating to science, industry, and education, find effective expression;
- (3) Taking such action as may be necessary to promote the application of science to our industries and to the service of the nation;
- (4) Discussing scientific questions in which international co-operation seems advisable.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 16, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Preliminary Report on the Purbeck Characæ." By C. REID, F.R.S., and J. GROVES.

"Notes on the Genus *Toxoplasma*, with a Description of Three New Species." By Prof. H. G. PLIMMER, F.R.S.

"The Convolutional Pattern of the Brains of Identical Twins; a Study on Hereditary Resemblance in the Furrows of the Cerebral Hemispheres." By F. SANO.

THE INSTITUTION OF MINING AND METALLURGY.

PRESIDENTIAL ADDRESS BY SIR R. A. S. REDMAYNE, K.C.B.

LET me thank you very sincerely for the honour you have conferred upon me in electing me your President for the ensuing year, an honour which I greatly appreciate. It will be my earnest endeavour to follow the good example set me by my distinguished predecessors in the Presidential Chair.

I propose to take as the subject of my address to-day the British Mining Industry in relation to the war, and to dwell on some phases of the question which impress me as of pre-eminent importance. I desire at the outset to make it quite clear that I am not now addressing you in my capacity of Chief Inspector of Mines, but as a mining engineer desirous of ventilating some matters which we engineers consider of great moment, and of trying to solve some problems in connection with mining which now more than ever are of national importance. I trust my remarks may be taken as being suggestive rather than dogmatic.

1. The Effect of the War on the Economic Position of the Country.

To state that we are engaged in the greatest war of all time has become a platitude, but it is the fact that colours all our thoughts and affects all our actions at the present time. We are pouring out life and treasure as never before in the history of the nation, not to secure a material return but to maintain our hard-won liberties and the rights of small nations to exist. War is the most wasteful of all human activities. The present prosperity that we witness in many industrial undertakings is a purely fictitious prosperity, and in the true meaning of the phrase is non-productive of wealth, for these industrial concerns are employed either directly or indirectly, to greater or less extent, in the production of the engines of war—war, the great destructor.

One result of the war is I think obvious: it will be followed by a period, longer or shorter, of industrial depression, amounting possibly to something like prostration, but I believe also that we have it within our power to remedy matters in a comparatively short period, and to put the nation on a stronger financial and industrial basis than ever before in its history. We must take time by the forelock and make our plans now.

In this connection reference may be made to the opinion of so great an authority on matters of industry as the President of the Board of Trade, who in a remarkable and inspiring speech delivered in the House of Commons on January 10 last said (I do not give the statements in the order in which they appear in his speech):—

"Recuperation is undoubtedly and will be one of the first necessities of the whole of Europe"; again, "The exhaustion from which all the belligerents will undoubtedly suffer will lead to a period of great effort, and I hope in all of them—I say without distinction 'in all of them'—to a greater degree of recuperation"; and again, "I believe we have it within our capacity to make up for the vast losses which we have incurred in a shorter period of time than any other State."

The President spoke of industrial enterprise in general, but mining, which is our second greatest industry—for I suppose we must put agriculture first—should be made to contribute more to industrial regeneration and advancement.

The war has emphasised one outstanding fact, viz., that we should and could approximate more closely to the ideal state of being self-supporting; in other words, develop to the utmost our natural resources and put them to the most economical use at home.

2. An Inventory of the Mineral Resources of the Empire Desirable.

Great Britain, and more especially England, is the most highly mineralised area in the world. No other country contains such a variety of mineral resources of use to mankind, not even the United States of America. Other countries may contain vastly greater quantities of one or more of the useful minerals, but no country so many and so varied. If we extend our view and intake the whole British Empire there is no fuel, ore, stone, or clay which is not contained therein. Mr. Runciman has said:—

"There should be no essential article either for the arts of peace or for the arts of war upon which we cannot without the Empire lay our hands."

He said further:—

"In the course of the afternoon reference has been made to the production of raw material in this country. The control of metals passed to Frankfurt years ago. It was Frankfurt that really dictated the production of metals in many parts of the world. Even in our own Dominions the influence of Frankfurt in Australia was so great that the Australian Government went to the extreme length of cancelling by legislation every contract on the outbreak of the war in which the great metal organisation of Frankfurt was concerned. We have control within the British Empire of some of the most valuable metals on which we now depend—manganese from India, tungsten from the Antipodes, zinc in large quantities from Australia, and nickel very largely from Canada. I should like to say, so far as these metals are concerned, that nothing could have been more whole-hearted than the support which has been given to us by the Dominions. Long ago, at the beginning of the war, we pointed out to them how largely we were dependent on them, and how short our supplies might be if they were dissipated too widely, and they at once, without any hesitation, took the most drastic action, so that we have an abundance of manganese here, tungsten we can get now in sufficient quantities, zinc is being produced in increasing quantities every month."

It behoves us therefore to know exactly where we stand in respect of our mineral resources—where the different kinds of minerals occur, of what quality, and to what

extent. A great deal of information exists on the subject in the "Transactions" of various technical institutions, in geological memoranda, and in reports on mining properties, which in the hands of a body of mining experts could be summarised so as to form part of a large work resulting from further inquiry and investigation. Would not the services of our Institution be of value in the prosecution of such an idea?

British Mineral Resources.

(a) Extensions of the Coalfields and Prevention of Waste in the Getting and Utilisation of Coal.

Passing from the wider subject let us limit our consideration to the mineral resources of the United Kingdom. Our most important mineral asset is of course coal, the next in importance being iron ore. An estimate of the available resources of coal was made by the Royal Commission on Coal Supplies, which reported in 1905, but since that date our knowledge in respect of the available resources of coal has been considerably enlarged.

The extensions—then of a somewhat speculative character—of the Notts and South Yorkshire fields have been proved, and the limits are now roughly known. The compass of the Kent coalfield has been more correctly determined and extensions of the Warwickshire field have been proved. Geologists are now not only speculating on the continuation of the Warwickshire and Staffordshire coalfields, but as to the probability of the existence of an entirely hidden coalfield in Southern England. Much, however, yet remains to be done in the way of exploratory work. Thus the eastern and western limits of the Warwickshire field have not yet been determined. In respect of the Staffordshire coalfields west of Birmingham the area between Wolverhampton and Shifnal remains to be proved, and I incline to the belief that in the latter area there are considerable deposits of coal. Another large and apparently profitable area of investigation is in Lancashire, where there is every reason to believe that there lies immediately under the red rocks to the south-west of Manchester a very large tract of middle coal measures, "the accessibility of which depends only on the thickness of the permo-triassic cover." Much good work could be done here by correlation of existing information, but the area is so complicated by faults and the like that borings would seem to be absolutely necessary to satisfactorily prove the value of the extension of the coalfield in this direction. Coming south many borings have been put down round and to the north of London—well into Buckinghamshire—and the underground geology of this area is broadly known. But to the west, viz., the area between London and Bristol, remains unproved.

Dr. Watts in his Presidential Address to the Geological Society in June, 1912, drew attention to this subject, pointing out that in Eastern and Southern England there exists "an area of Palæozoic rocks unconformably covered by Neozoic rocks larger in extent than the uncovered Palæozoic outcrop of England and Wales." Exploration has not proceeded far, and he argued that the time had come "for the organisation of a systematic survey of this area by means of a considered series of borings, so planned as to investigate the structure of the concealed Palæozoic floor, to ascertain the thickness of cover, to locate any coal basins which may form part of the floor, and to elucidate their exact tectonic conditions in order to determine their suitability for profitable working."

It is eminently desirable that further extensions of our coalfields should be defined, and hidden fields if they exist be discovered, to replace the dying fields of South Staffordshire, Bristol, and elsewhere. It is to my mind essential that the exploratory work necessary to prove the areas indicated should be placed in the hands of persons thoroughly competent in respect of both geological and engineering knowledge.

Desirable as it is that we should know the extent of our

coal resources, it is equally so that we should know more, concerning the calorific and chemical values of the various coals at present being worked. We are sadly lacking in information in this respect. Not only is it probable that many of the existing chemical analyses are incorrect in some details—not intentionally incorrect, but faulty methods of analyses have been adopted ("The Geological Structure of the South Lancashire Coalfield," by George Hickling, D.Sc., F.G.S., *Trans. Inst. Min. Eng.*, 1, 11., 228) (recent investigation by the Departmental Committee on Spontaneous Combustion of Coal in Mines leads one to the conclusion that the exact chemical analysis of coal is little understood)—but the information available requires to be correlated, systematised, and extended, in order that the coalfields may be mapped out area by area according to similarity of quality, in order that a chemical survey of the coal areas may be accomplished. Such a survey, constituting as it would a complete compendium of chemical and metallurgical knowledge in respect of our fuel supplies, would be of great value to consumers and form the basis of a further enquiry, to which allusion will presently be made.

In connection with the national coal supply, two main questions which suggest themselves for answer are:—

(1) Is the conclusion of the Royal Commission on Coal Supplies, to the effect that the rate of increase of output will become lower, remain stationary, and then decline, sufficient ground for not taking steps to conserve our coal supplies?

(2) Should not prevention of wastage and not restriction of output or (except in abnormal times) restriction of export be aimed at; would not considerable advantage result from the appointment of a Standing Committee of experts to advise on the subject from time to time on—

(a) The rate of exhaustion.

(b) Duration of supplies.

(c) As to steps to be taken (1) to conserve, (2) to utilise to the best advantage to the nation the remaining supplies?

I think these queries may be replied to as follows:—

As to (1)—The conclusion arrived at by the late Commission on Coal Supplies in respect of the probable "curve of production" is not sufficient ground for assuming that no steps are necessary for the conservation of coal.

As to (2)—The appointment of a small Standing Committee of experts to advise on the subject from time to time has I believe been mentioned before now, and is worthy of serious consideration, though there would be difficulties in the way of its being an effective committee. The first two of the items which such a committee would have to investigate—viz., the rate of exhaustion and duration of our supplies of coal—present small difficulty, but the steps which should be taken to conserve and utilise to the best advantage the remaining supplies, the prevention of waste in "getting" and waste in "using" coal, bristle with difficulties.

Some sources of waste in getting coal and means for the reduction of waste in working coal may be noticed:—

(1) Certain portions of seams at present being worked are left in the goaf (gob or waste). This coal may be of an inferior quality to that portion of the seam which is sent out of the mine, and more difficulties might in some cases result were the whole of the seam extracted. In some cases, however, the coal left is not of bad quality and if left in the waste can be recovered.

One case may, perhaps, be given of wastage in getting coal which is taken from Part II. of my Annual Report to the Secretary of State for the year 1910:—

"The Yorkshire coalfield is now being rapidly extended, the chief developments taking place in the neighbourhood of Doncaster, namely, on the eastern boundary of the working field. Mr. Pickering (late Inspector of Mines in charge of the Yorkshire and North Midland Division) in his Report for 1910 gives an interesting map illustrating the proved and estimated areas of the coalfield. Several collieries near Doncaster have now very large outputs

and several new winnings are being made and others are in contemplation. The Barnsley bed is the chief coal seam in the district, a typical section showing 9 ft. 5 ins. of coal. . . . The seam occurs at a great depth, varying within a few miles from 550 yards to 950 yards, and unfortunately it is a gassy seam. Experience has also shown it to be subject to spontaneous combustion. This is a combination of circumstances which must be viewed with anything but complacency, and is one which will require in future the exercise of the greatest care and most efficient management.

"At several of these mines nearly half of this fine seam is left unworked, the 'top-softs,' about 4 feet thick, being left to fall in the goaf. This part of the seam is not of such high quality as the bottom portion, and that is the chief reason for it being left unworked. One characteristic of this portion of the bed is that it is moist gassy and fiery, and there can be no doubt that the fact of its being left in the waste contributes to the dangerous state of things referred to.

"To lose practically 40 per cent of this seam is also a national loss. Attempts have been made at several collieries to work the top coal as a second face, in the goaf, with some success, at least 60 per cent of the top-softs being easily obtained. At other collieries practically the whole of the coal is obtained and fewer gob fires result."

Is it too much to hope that means may be devised whereby this loss of coal may be prevented and to render its use profitable?

(2) It sometimes arises that when two seams are close together that of highest quality is worked first, and in consequence it may be that much damage is done, with attendant loss of coal, in respect of the seam or seams of poorer quality. From a national point of view the order of working should be determined with a view to causing as little total loss as possible.

(3) The Royal Commission on Coal Supplies had evidence "brought before them that much coal had been and is lost through the practice of leaving unnecessary barriers between royalties and properties, but the present tendency to take large areas under lease is reducing the loss from this cause, and in many cases barriers between properties are now worked out by mutual agreement." Much more might be done in this direction.

(4) In the past extensive areas of partially worked coal have been temporarily or entirely lost through indiscriminate working—e.g., in the Black Country (South Staffordshire). By the erection of central pumping stations such areas can and have been to some extent recovered. Means should be taken to ensure that in the future there is no recurrence of such unsystematic and wasteful mining.

(To be continued).

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

At the third Annual General Meeting, held at the London Chamber of Commerce on the 22nd inst., Sir Boverton Redwood, Bart., D.Sc., F.R.S.E., retiring from the Presidency in conformity with the by-laws (after two years' tenure of that office), referred to the meritorious public services of his successor, Prof. John Cadman, C.M.G., D.Sc., M.Inst.C.E., and congratulated him upon the honour recently conferred upon him in being made a Companion of the Order of St. Michael and St. George. In taking the Chair, Prof. Cadman paid an eloquent tribute to the abilities of his predecessor, employed unreservedly in the interest of his country as technical adviser of several departments of the Government, and remarked that the foundation and subsequent success of the Institution were largely due to Sir Boverton's energetic action.

The Vice-Presidents and Council for the ensuing year are:—

Vice-Presidents—The Rt. Hon. Lord Cowdray of Midhurst; Sir Thomas H. Holland, K.C.I.E., D.Sc., F.R.S.; and Sir Boverton Redwood, Bart., D.Sc., F.R.S.E.

Council—Alfred G. Adams; Herbert Allen; Sir Robert Ballour, Bart., M.P.; Capt. R. W. Barnett, M.A.; Herbert Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A.; George T. Beilby, I.L.D., F.R.S.; Edwin R. Blundstone, B.A., F.C.S.; Andrew Campbell; John T. Cargill; Major A. Cooper-Key, C.B.; E. H. Cunningham Craig, B.A., F.G.S.; Arthur W. Eastlake, M.Inst.M.E., A.M.I.Mech.E.; C. Greenway; T. C. Palmer, Assoc.M.Inst.C.E.; F. Mollwo Perkin, Ph.D., F.I.C., F.C.S.; and Robert Redwood, F.C.S.

NOTICES OF BOOKS.

Sulphuric Acid and Sulphur Products. By GEOFFREY MARTIN, D.Sc. (Bristol), D.Sc. (London), Ph.D., F.C.S., and Major J. LOUIS FOUCAR, B.Sc. (London). Pp. viii.+80. Price 7s. 6d. net. London: Crosby Lo.wood and Son. 1916.

THE authors of this book claim to have brought together most of the available data concerning the manufacture of sulphuric acid and industrial sulphur compounds, but it has been compressed to such an extent as to impair very considerably the value of the information. A short account is first given of the sulphur industry, including the extraction of natural sulphur, and the recovery of sulphur by the Chance and Claus, Thiogen, and other processes. These accounts are hardly fuller than those to be found in the ordinary fairly advanced text-book of inorganic chemistry, but a good bibliography is provided and some references to current literature. The preparation of sulphuric acid is next taken up, and here rather more detail is given, though not by any means enough for the specialist, and only brief allusion is made to some branches. Other sulphur compounds treated of include sulphur dioxide and sulphites, carbon disulphide, sodium thiosulphate, &c., but, again, the average text-book would provide almost as much detail as is to be found here.

Field Analysis of Minerals. By G. D. McGRIGOR. London: *The Mining Magazine*. 1915. Pp. 88. Price 3s. 6d. net.

THIS useful book is based upon tables of the reactions of the elements compiled by the author when a student, and much used by him since in practical work in the field. The results of some years of experience have been incorporated in the text, and some additions have been made to the tables. The author wisely recommends the use of physical, dry, and wet tests in conjunction in the examination of minerals, and describes only those methods which can be employed in the field with the simplest equipment. Prospectors and travellers will readily realise the great convenience of having one book by the aid of which they can identify all common minerals, and which contains no matter which is useless for their purpose, and the author is no doubt justified in claiming with this book in his possession the traveller will require but very little instruction or help in chemical analysis. An abstract of the article by the late Sir Warrington Smyth on the use of the blowpipe, which was prepared for the fourth edition of the "Admiralty Manual of Scientific Enquiry," is included, with some notes and comments by the author.

Recent Researches in the Wolcott Gibbs Memorial Laboratory of Harvard University. By THEODORE W. RICHARDS.

THIS Address, given before a meeting of the National Academy of Sciences at New York in November, 1915, and reprinted from *Science*, vol. xli., contains an account of the researches which have been carried out in the

Wolcott Gibbs Laboratory in the three years it has been in existence. The account is prefaced by a brief description of the building and equipment, which shows it to be one of the best planned in the world. During the past three years 24 papers have been published, while many others are almost finished. Although the researches described are of varied character and scope they have one common aim—the study of the fundamental properties of the chemical elements, including atomic weights, electromotive behaviour, densities and compressibilities, heat of combination with one another, and the physical and chemical properties of their compounds. Many important advances in our knowledge have been the outcome of the work done in the Wolcott Gibbs Memorial Laboratory, and the whole scientific world owes a debt of gratitude to its founder, Dr. Morris Loeb, the pupil of Gibbs, and to its able and highly endowed director.

Special Reports on the Mineral Resources of Great Britain. Vol. III. *Gypsum and Anhydrite.* By R. L. SHERLOCK, D.Sc., and B. SMITH, M.A., and *Celestine and Strontianite*, by R. L. SHERLOCK, D.Sc. London: Printed under the Authority of His Majesty's Stationery Office. 1915. Price 1s. Pp. iv. + 57.

This report deals with the properties, uses, treatment, and modes of occurrence of the sulphates of calcium and strontium. Statistics of the annual output of the United Kingdom are given, and all the important mines and quarries were visited by the authors in order that reliable information might be obtained as to the working of them. The physical properties of gypsum and anhydrite, and of celestine and strontianite are described, and an outline is given of their uses and treatment. Hitherto the greater part of the celestine mined in this country, after being hand-cleaned, has been exported to Germany for further treatment, but the authors state that works for its treatment in this country are in contemplation.

Special Reports on the Mineral Resources of Great Britain. Vol. II. *Barytes and Witherite.* By R. G. CARRUTHERS, T. EASTWOOD, A.R.C.S., G. V. WILSON, B.Sc., R. W. POCOCK, B.Sc., and D. A. WRAY, B.Sc. London: Printed under the Authority of His Majesty's Stationery Office. 1915. Price 1s. 6d.

THE Director of the Geological Survey is preparing a series of special reports upon the mineral resources of Great Britain, in response to many enquiries which have been made on the subject since the beginning of the war. This second volume deals with the sulphate and carbonate of barium, of which all but the highest qualities are found in abundance in Great Britain. Before the war more than half the barium salts used in this country were imported, chiefly from Germany, the products from the latter country being of specially good colour and finely ground. It would appear to be by no means impossible to improve the methods of preparation of the home product, and it is to be hoped that the opportunity which now occurs of doing so profitably will be seized. The report gives an account of the properties and industrial uses of the minerals, and also contains detailed descriptions of all the barium mines of Great Britain, both working and abandoned.

MISCELLANEOUS.

High Prices for Acetic Acid.—Amongst the commodities that have appreciated in price during the war is acetic acid. In the Federated Malay States, where it is used for the coagulation of the latex of the rubber tree, the price was 16s. 4d. per jar before the war. In January last it was quoted at £4 1s. 8d. per jar, and last month at £5 16s. 8d.

Physical Constants of Chlorine.—Maurice Pellaton. —The author has determined the critical temperature of chlorine by the optical method, obtaining the value $t_c = 144.0^\circ$. He has also determined the vapour tensions of liquid chlorine from -80° to the critical temperature. From -80° to 0° he used Krietsch's method with a mercury manometer, the meniscus being separated from the chlorine gas by an index of concentrated sulphuric acid, and from 0° to 144° he used a special method. The value he obtained is $p_c = 76.1$ at. The density of liquid chlorine at its critical temperature is $\Delta = 0.573$. The latent heat of vaporisation of liquid chlorine has been calculated from 0° to 144° . All the author's determinations seem to prove that chlorine gas behaves like a normal substance.—*Jour. Chimie Physique*, [4], xii., 426.

Movement of Ions (and Electrons) in an Electric and Magnetic Field.—Auguste Righi. —A detailed experimental investigation of the various phenomena due to the action of a magnetic field upon an ionised gas has led the author to formulate an electronic theory of electromagnetic forces capable of moving a weight; that is to say, forces which set in motion a conductor traversed by a current when a magnetic field of any origin acts upon it. In this article the author gives the general formulae relating to the movement of charges under the action of an electric field and a magnetic field, both being uniform, and then applies the formulae to elucidate various phenomena. His experiments on the mechanical effects produced by a magnetic field in ionised gases has led him to conclude that the ions and electrons in a gas traversed by a current by their blows upon the walls of the tube exercise a pressure the resultant of which is zero. But if there is a magnetic field the resultant displaces the tube, supposed movable, exactly as if there were in place of it a conductor traversed by the same current; this is due to the change of form of the trajectories of the ions and electrons between one blow and another. The electronic theory of forces capable of moving weights admits that the forces are the effect of pressures exercised by the mobile electrons in the interior of conductors. These blows affect the molecules which thus play the part of walls.—*Annales de Physique*, 1915, 9th Series, vol. iv.

MEETINGS FOR THE WEEK.

- MONDAY, April 3rd.—Royal Institution, 5. (General Meeting).
Royal Society of Arts, 4.30. (Fothergill Lecture).
"Surveying—Past and Present," by E. A. Reeves.
- TUESDAY, 4th.—Royal Institution, 3. "Modern Horticulture—Growing Time and Seed Time (Internal Rhythm)," by Prof. F. Keeble.
- Röntgen Society, 8.15. "Chronograph constructed to Work with the Electroscope," by P. J. Neate.
"The Enclosed Tungsten Arc as a Source of Ultraviolet Light," by B. H. Morphy and S. R. Mullard.
"Experiments with a Coolidge Tube," by E. Schall.
"New Modification of the Ionisation Method of Measuring X-rays," by H. E. Donithorne. Exhibition of Plates showing Experiments with the Coolidge Tube in Radiography.
- WEDNESDAY, 5th.—Royal Society of Arts, 4.30. "Painting by Dipping, Spraying, and other Mechanical Means," by Arthur S. Jennings.
- Society of Public Analysts, 8. "Alkalimetric Estimation of certain Bivalent Metals in the Form of Tertiary Phosphates," by W. R. Schoeller and A. R. Powell. "Specimen of Russian Oak," by P. A. Ellis Richards. "The Estimation of Potassium in presence of other Substances," by A. H. Bennett.
- THURSDAY, 6th.—Royal Institution, 3. "English Music in the Tudor Period—Secular Part Music," by Dr. W. H. Hadov.
- Faraday Society, 8. "The Making of a Big Gun" (illustrated by Cinematograph Pictures), by Dr. W. Rosenhain.
- Chemical, 8. "A Space Formula for Benzene," by J. N. Collie. "New Form of Distilling Flask, together with a Note on Benzyl Benzoate," by Earl of Berkeley. "3-Phenanthrolyl-4-aldehyde," by J. W. Smith.
- FRIDAY, 7th.—Royal Institution, 5.30. "Plea for War," by W. S. Lilly.
- SATURDAY, 8th.—Royal Institution, 3. "Radiations from Atoms and Electrons," by Sir J. J. Thomson.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2941.

THE ESTIMATION OF URANIUM AND PHOSPHORUS.

By H. D. NEWTON and J. L. HUGHES.

It has been shown by Newton (*Am. Journ. Sci.*, 1908, xxv., 343) that ferric iron in sulphate solution can be quickly and accurately estimated by reducing with titanous sulphate, oxidising the excess of titanous salt with bismuth trioxide, filtering off the excess of bismuth trioxide and reduced bismuth, and titrating the resulting clear solution with a 0.1N solution of potassium permanganate. As it was afterwards discovered that uranyl salts in sulphate solution were apparently reduced by titanous sulphate to the uranous condition, the present investigation was undertaken for the purpose of applying the above method to the estimation of uranium and to the estimation of phosphorus after the latter had been precipitated as ammonium-uranyl phosphate.

For this work a solution of titanous sulphate of convenient strength was prepared as follows:—To 100 cc. of sulphuric acid were added little by little and with continual stirring 25 gm. portions of the best hydrous c.p. titanium oxide, the whole being kept constantly heated to the fuming-point of the acid. The resulting pasty mass was allowed to come to room temperature and cautiously transferred to a beaker containing about 200 cc. of cold water. After standing a short time the somewhat cloudy solution of titanic sulphate was filtered, reduced to the titanous condition by means of zinc, and then filtered directly into about two litres of recently boiled distilled water, contained in a reservoir to which a Squibb's automatic burette and a hydrogen generator were immediately attached. By this means the easily oxidised titanous sulphate was kept under a constant pressure of hydrogen, and measured amounts of the solution were drawn as wanted. As it was convenient to know the strength of the titanous sulphate solution it was titrated directly against a 0.1N solution of potassium permanganate.

An approximately 0.1N solution of uranyl sulphate was obtained by treating an equivalent amount of uranyl acetate of tested purity with sulphuric acid, filtering, and diluting to the required volume. This solution was standardised in the gravimetric way by precipitating the uranium by ammonia, washing with dilute ammonium nitrate solution, igniting, and weighing as U_3O_8 .

A phosphate solution was obtained by dissolving about 6.359 grms. of microcosmic salt in a litre of water, the solution being afterwards standardised by use of the magnesium pyrophosphate method as outlined by B. Schmitz (F. P. Treadwell's "Analytische Chemie," 1911).

The potassium permanganate solution of approximately 0.1N value was exactly standardised by titrating against carefully weighed portions of purified sodium oxalate previously dissolved in a convenient volume of water, acidulated with 1:1 sulphuric acid, and heated to 80°. This method is the one recommended by the Bureau of Standards when using sodium oxalate as a standard in volumetric analysis, and is exactly described in their Circular, No. 40. The sodium oxalate here used was kindly furnished by the above-mentioned Bureau.

A bismuth trioxide must be taken which shows no appreciable reducing action toward potassium permanganate. A number of 2 gm. lots of the sample used, when dissolved in sulphuric acid, cooled, and diluted, were permanently coloured by the first drop of a 0.1N solution of potassium permanganate.

The Estimation of Uranium.

In preliminary experiments it was found that bismuth trioxide had no appreciable oxidising action on uranous salts. Table I. contains results obtained by titrating with permanganate the uranous solution left after reducing with zinc a measured amount of uranyl sulphate, cooling, adding a gm. of bismuth trioxide, and filtering.

TABLE I.—Data showing Lack of Oxidising Effect of Bismuth Trioxide on Uranyl Sulphate.

KMnO ₄ used.	UO ₂ present.	UO ₂ found.	Error.
Cc.	Grm.	Grm.	Grm.
8.01	0.1083	0.1088	+0.0005
7.91	0.1083	0.1074	-0.0009
7.97	0.1083	0.1082	-0.0001
7.98	0.1083	0.1084	+0.0001
7.93	0.1083	0.1077	-0.0006
8.00	0.1083	0.1086	+0.0003
7.95	0.1083	0.1080	-0.0003

In Table II. are recorded results obtained when titanous sulphate was used as the reducing agent. For these experiments measured amounts of uranyl sulphate were run into an Erlenmeyer flask of 150 cc. capacity and followed by a slight excess of titanous sulphate solution. Enough concentrated sulphuric acid was then added to make the solution approximately 16 per cent acid by volume. (It was found that uranyl salts are more easily reduced and when reduced much more stable in an acid solution of this concentration than in one that is weaker). The flask and contents were then cooled under the tap, a small amount of bismuth trioxide was added (enough in each case to oxidise the excess of titanous sulphate), and the flask then left to stand a minute or two, with occasional shaking. By the use of the filter pump and a platinum cone well padded with asbestos the solution was quickly filtered free from bismuth trioxide and reduced bismuth, the asbestos pad carefully washed three or four times with a 16 per cent sulphuric acid solution, and the combined filtrates titrated with standard potassium permanganate. As the titanous sulphate solution contained a small amount of iron a slight correction had to be made in the permanganate reading. This correction was easily and accurately made by a method of estimating iron in the presence of titanium, as worked out by Gooch and Newton (*Am. Journ. Sci.*, 1907, xxiii., 365).

TABLE II.—Data on Titration of Uranium After Reduction by Titanous Sulphate in Presence of Bismuth Trioxide.

KMnO ₄ used.	UO ₂ present.	UO ₂ found	Error.
Cc.	Grm.	Grm.	Grm.
4.03	0.0541	0.0545	+0.0004
4.06	0.0541	0.0549	+0.0008
8.06	0.1083	0.1092	+0.0009
8.03	0.1083	0.1088	+0.0005
7.96	0.1083	0.1079	-0.0004
12.03	0.1624	0.1631	+0.0007
12.00	0.1624	0.1626	+0.0002
12.00	0.1624	0.1626	+0.0002
12.00	0.1624	0.1626	+0.0002
16.03	0.2166	0.2173	+0.0007
16.00	0.2166	0.2169	+0.0003
16.03	0.2166	0.2173	+0.0007
16.03	0.2166	0.2173	+0.0007

As 1 cc. of 0.1N permanganate corresponds to 0.01350+gm. of uranium dioxide and one drop or one-thirtieth of a cc. corresponds to 0.00045+gm. of uranium dioxide, it appears that any appreciable error in the process is probably due to the reading of the end-point.

The Estimation of Phosphorus.

It has long been known that under proper conditions an alkali phosphate is completely precipitated by adding to it an excess of uranyl nitrate. In using the above reaction for the estimation of phosphorus when a separation of the

ammonium-uranyl phosphate is involved the process of filtration has always been the principal difficulty. In fact E. F. Kern made the statement that owing to its extreme fineness ammonium-uranyl phosphate could not be filtered successfully through a Gooch crucible (*Journ. Am. Chem. Soc.*, 1901, xxiii., 710). Pulman (*Am. Journ. Sci.*, 1903, xvi., 229) in his paper on "The Estimation of Uranium and Uranyl Phosphate," which involved the filtering of the finely divided ammonium-uranyl phosphate, after giving Kern's statement, wrote of his own experience as follows:—

"It was found that the precipitate went through two ashless filter papers (Schleicher and Schüll, No. 589), and also that an asbestos felt of ordinary tightness in a Gooch crucible would not entirely retain the precipitate. By shaking up the flask containing the asbestos, however, allowing it to settle a minute, and then pouring off the particles still in suspension a very finely divided asbestos was obtained, which when poured upon the felt made in the ordinary way was found to give a pad of such tightness that the filtrate obtained from the ammonium-uranyl phosphate was perfectly clear."

And in conclusion he writes:—

"The only objection to the process is that the filtering and washing of the precipitate are apt to be slow, especially when large amounts of the material are being treated."

When using the Gooch crucible our experience was similar to that of Pulman, two to three hours being sometimes needed to complete the filtering process when larger amounts of microcosmic salt were taken for analysis. It was thought that a perforated platinum cone lined with an asbestos felt would allow of faster filtering and still retain the finely divided ammonium-uranyl phosphate. A few experiments with a 2.5 inch cone sufficed to show that not only did the liquid filter much faster, but also that it was not necessary to use an extremely fine asbestos, because the ordinary asbestos as usually prepared for the Gooch crucible (when put on with some care) answered the purpose quite as well. With the help of this filtering cone experiments were carried on in the effort to adapt the previously described method for the estimation of phosphorus.

TABLE III.—Indirect Determination of Phosphorus in Ammonium-Uranyl Phosphate.

KMnO ₄ used. Cc.	UO ₃ equiv. to P ₂ O ₅ present.		UO ₃ found.		P ₂ O ₅ present.		P ₂ O ₅ equiv. to UO ₃ found.		Error on P ₂ O ₅ Grm.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	
3.3	0.0477	0.0470	0.0470	0.01183	0.01183	0.0116	—0.0002		
3.35	0.0477	0.0479	0.0479	0.01183	0.0118	—			
3.35	0.0477	0.0477	0.0477	0.01183	0.0118	—			
3.33	0.0477	0.0474	0.0474	0.01183	0.0117	—			
3.3	0.0477	0.0470	0.0470	0.01183	0.0116	—0.0002			
6.7	0.0954	0.0959	0.0959	0.02367	0.0237	+0.0001			
6.65	0.0954	0.0952	0.0952	0.02367	0.0236	—			
6.63	0.0954	0.0949	0.0949	0.02367	0.0235	—0.0001			
6.63	0.0954	0.0949	0.0949	0.02367	0.0235	—0.0001			
9.95	0.1431	0.1428	0.1428	0.03550	0.0354	—			
9.95	0.1431	0.1427	0.1427	0.03550	0.0353	—0.0001			
9.95	0.1431	0.1427	0.1427	0.03550	0.0353	—0.0001			
13.26	0.1909	0.1903	0.1903	0.04734	0.0472	—0.0001			
13.33	0.1909	0.1913	0.1913	0.04734	0.0474	+0.0001			
13.3	0.1909	0.1909	0.1909	0.04734	0.0473	—			

The process as finally adapted is as follows:—A measured amount of standard microcosmic salt solution was drawn into a 250 cc. beaker and a mixture of 10 grms. of ammonium acetate, freshly prepared by neutralising concentrated ammonium hydroxide with 50 per cent acetic acid and 5 cc. of glacial acetic acid, was added. The volume was then made up to 150 cc. and the solution heated nearly to the boiling point. An excess of uranium nitrate was then slowly added with constant stirring,

after which the beaker and contents were kept heated nearly to the boiling-point for half an hour. After cooling to room temperature the resulting ammonium-uranyl phosphate (UO₂NH₄PO₄) was filtered on an asbestos felt contained in the platinum cone, which had been previously moistened with a 2 per cent solution of ammonium acetate. After carefully washing the precipitate with the 2 per cent ammonium acetate solution the cone and contents were transferred to a funnel of convenient size, and the precipitate was dissolved and washed into a 150 cc. Erlenmeyer flask with the use of a 16 per cent solution of sulphuric acid. This solution was then treated in turn with titanous sulphate and bismuth trioxide and titrated with potassium permanganate, exactly as described in the process for the estimation of uranium. The results obtained are given in Table III.—*Journal of the American Chemical Society*, xxxvii., No. 7.

THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES.*

By ROGER C. WELLS.

(Continued from p. 151).

SULPHIDES (continued).

Experiments with the Sulphates of Copper and Zinc.

A good illustration of selective precipitation was obtained with mixtures of cupric sulphate and zinc sulphate, precipitated by ammonium sulphide. The data are given in the table below and the curves in Fig. 1. The evidence is

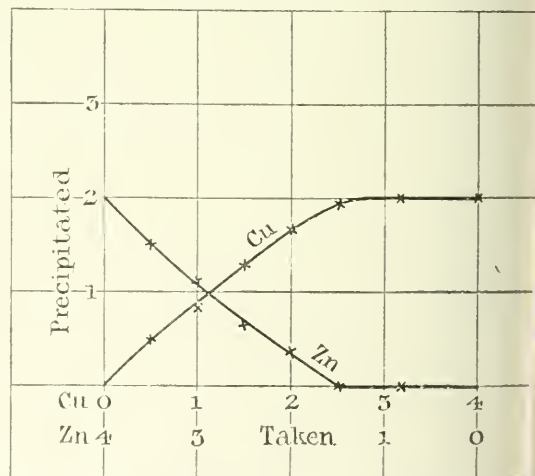


FIG. 1.—Selective precipitation of copper before zinc by ammonium sulphide. The abscissæ represent the content of the solution in mgm. equivalents of cupric sulphate and zinc sulphate before the addition of 2 mgm. equivalents of ammonium sulphide; the ordinates represent the composition of the resulting precipitate.

very clear that even in alkaline solution more cupric sulphide is precipitated than zinc sulphide. The quantities of substances used are expressed in mgm. equivalent (See ante). The solutions were dilute at the time of precipitation, the final volume being 40 cc. for the quantities stated in the table.

* Bulletin 609, United States Geological Survey.

Fractional Precipitation of Cupric and Zinc Sulphates by Ammonium Sulphide.

(2.00 mgrm. equivalents in each precipitation).

Cupric sulphate. taken. Mgrm. equivalents.	Zinc sulphate taken. Mgrm. equivalents.	Copper in precipitate. Mgrm. equivalents.	Zinc in precipitate. Mgrm. equivalents.
0.00	4.00	0.00	2.00
0.50	3.50	0.49	1.51
1.00	3.00	0.87	1.13
1.50	2.50	1.29	0.60
2.00	2.00	1.70	0.41
3.00	1.00	1.97	0.02
3.20	0.80	2.05	0.00
4.00	0.00	2.00	0.00

These results are stated fully as illustrations of relations which hold for most pairs of sulphides. Both precipitate together at first, then one largely redissolves, leaving the sulphide radicle in combination with a single metal.

These facts may find application in theories of the formation of ores. If large bodies of precipitable solutions come into sudden contact, an indefinite mixture of sulphides will be precipitated. On the other hand, if the solutions are somewhat warm or react slowly the sulphides tend to be precipitated in a definite succession.

Work of Anthon and Schürmann.

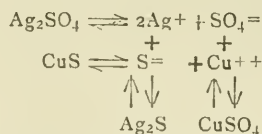
The precipitation of soluble salts of metals by the insoluble sulphides of other metals was studied long ago by Anthon (*Journ. Prakt. Chem.*, 1837, x., 353). He obtained the series silver, copper, lead, cadmium, iron, nickel, cobalt, and manganese. A sulphide of any one of these metals, he found, would be precipitated at the expense of the sulphide of one lower in the series. The subject was studied further in 1888 by E. Schürmann ("Ueber die Verwandtschaft der Schwermetalle zum Schwefel," *Liebig's Ann.*, 1888, ccxlix., 326), who enlarged the series as follows:—Palladium, mercury, silver, copper, bismuth, cadmium, antimony, tin, lead, zinc, nickel, cobalt, ferrous iron, arsenic, thallium, and manganese. The experiments of Anthon and Schürmann lead to exactly the same conclusions as those on fractional precipitation. The further investigation of sulphides was therefore restricted to some of the side issues involved. (See *prox.*).

Schürmann found that some of these transpositions, of which he studied a very large number, occurred more easily than others, particularly those where the metals are widely separated in the series. It was especially difficult to obtain complete transformations in the case of nickel sulphide treated with zinc sulphate, and between thallium salts and the neighbouring members of the series. The behaviour of iron was peculiar in that the sulphides of zinc, nickel, and cobalt formed at the expense of an excess of ferrous sulphide, but they were in turn dissolved when treated with ferrous sulphate. The positions of arsenic, tin, and antimony in the series are subject to qualifications depending on the valence of the metal.

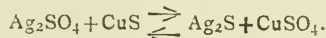
This series for the order of solubility of sulphides has thrown great light on the development of sulphide ores (W. H. Emmons, "The Enrichment of Sulphide Ores," *Bull.* 529 U.S. Geol. Survey, 1913, p. 56). It indicates the order of deposition of sulphides from a mixture of metallic salts when they compete under equal conditions for a sulphide. The first metals of the series will be precipitated first, leaving the solution richest in the last members; or, if the solution is going on, the last members will tend, other things being equal, to go into solution first.

Schürmann was chiefly interested in determining the place of each metal in the series. He considered the series to represent the order of the "affinities" of the metals for sulphur. A more empirical statement is that it represents the order of the solubilities of the sulphides in water (R. C. Wells, *Econ. Geology*, 1910, v., 7).

If the mechanism of these reactions is considered according to present theories, we should have the following scheme of ionisation in solution, for example, for the couple silver-copper:—



Since the solubility product of silver sulphide smaller than that of copper sulphide, silver sulphide forms at the expense of copper sulphide, and the equilibrium lies well toward the right in the following equation:—



The actual relations may be more complex than the last equation indicates, because there may also be a reaction of oxidation and reduction, but the scheme shows the general relation. Every sulphide has a "solubility product"; that is, the product of the concentrations of its two ions, which must be exceeded before precipitation can occur. Conversely, if the concentrations of the ions of any sulphide are less than its solubility product the sulphide will dissolve. That Schürmann's series is very nearly the order of solubility of the sulphides in pure water is evident from a comparison of the last column in the table on page 151 with Schürmann's series above.

The idea of the solubility product allows us at once to explain certain facts noted by Schürmann and to predict others with reasonable confidence. For instance, it is not a matter of primary importance what acidic radicles are present in the solution as long as they do not form insoluble salts with the metals present. Again, the greater speed of adjustment of equilibrium for metals widely separated in the series accords with our present idea that the speed of reaction is a function of the remoteness of removal from equilibrium.

If we let K_1 and K_2 represent the solubility products of two sulphides involved in a fractional precipitation and write—

$$\begin{array}{l} K_1 = (M_1)(S) \\ K_2 = (M_2)(S) \end{array}$$

where (M_1) , (M_2) , and (S) represent concentrations of metal 1, metal 2, and sulphide ions, then when equilibrium is established, since the sulphide ion is common we should have—

$$\frac{K_1}{K_2} = \frac{(M_1)}{(M_2)} \text{ or } \frac{(M_1)}{(M_2)} = K_3, \text{ a new constant. (1).}$$

That is, the ratio of the concentrations of the two metallic ions in a solution saturated with both sulphides should be a constant, independent of the quantity of sulphides but probably somewhat dependent on the temperature. Schürmann, as a rule, gave only qualitative results, and where he says one metal was "completely" separated from the other more exact research might show that a distribution occurs. As a matter of fact, however, the relation expressed by Equation 1 above has not yet been experimentally illustrated in a quantitative way for sulphides.

A consideration of the solubility of sulphides helps to explain certain phenomena observed by Stokes ("Experiments on the Action of various Solutions on Pyrite and Marcasite," *Econ. Geology*, 1907, ii., 19). He found that pyrite and marcasite are slightly attacked by a solution of alkali carbonate but much more completely when a carbonate of copper, lead, silver, or zinc is present. This is no doubt due in part to the greater insolubility of the sulphides of copper, lead, silver, or zinc, which form at the expense of the sulphide of iron in the pyrite and marcasite while the alkali dissolves the excess sulphur, the two concurrent reactions being much more effective than either singly.

Compound Sulphides.

One of the objects in studying fractional precipitation was to gain light on the conditions of formation of compound sulphides, such as chalcopyrite. It is easy to perceive that the solubility of one sulphide might be changed by the presence of a second in solution, and that a compound sulphide might have an intermediate solubility, following the usual behaviour as described by van't Hoff for double salts. The sulphides are so insoluble, however, that no adequate study of their behaviour over a wide range of conditions has as yet been made.

Grout has suggested that compound sulphides may have been produced in some instances by the admixture of alkaline and acid solutions ("On the Behaviour of Cold Acid Sulphate Solutions of Copper, Silver, and Gold with Alkaline Extracts of Metallic Sulphides," *Econ. Geology*, 1913, viii.). This seems very probable. Malfatti has described certain complex sulphides of iron of the formula $RFeS_2$ where R is a univalent radicle ("Beiträge zur Kenntnis des Eisensulfids," *Zeit. Anal. Chem.*, 1909, xlviii., 352). But in chalcopyrite copper has usually been regarded as bivalent, if the formula is written $Cu_2S.FeS$; to write it $Cu_2S.Fe_2S_3$ suggests trivalent iron. However that may be, if chalcopyrite could be formed by a simple precipitative reaction its formation would remove the constituents from a solution in definite proportions. Such removal would modify curves like those shown in Fig. 1 into lines with horizontal sections over certain regions. As no such horizontal sections were discovered in the fractional precipitation of copper and iron sulphide the conditions for the formation of chalcopyrite were not revealed by that method (for details see *Econ. Geology*, 1910, v., 1). It was therefore concluded that the formation of chalcopyrite by a precipitative reaction at moderate temperature and pressure demands at least more precipitating sulphide than corresponds to the copper present; otherwise no iron will be precipitated. Further investigation of this subject is needed.

By microscopic examination of the lean Butte ores J. F. Simpson has shown that the pyrite contains the copper as the copper minerals chalcocite, bornite, chalcopyrite, and enargite, and that of such minerals chalcopyrite is the oldest ("The Relation of Copper to Pyrite in the Lean Copper Ores of Butte, Mon.," *Econ. Geology*, 1908, iii., 635). Graton and Murdock have reached similar conclusions after an examination of many specimens from other localities ("The Sulphide Ores of Copper," *Am. Inst. Min. Eng. Bull.*, May, 1913, pp. 741-812). The typical minerals of enrichment processes appear to have been formed by the progressive alteration of one mineral into another, not strictly a fractional precipitation, although the fractionating tendency is revealed by the removal of the iron and the increasing deposition of copper. For the formation of the compound sulphides by enrichment the iron sulphide is already present. Of course, chalcopyrite may also result from magmatic differentiation, but for aqueous solutions we cannot avoid the conclusion that its formation indicates the presence of an excess of available sulphide beyond the requirements of the copper. Briefly, a small amount of a soluble sulphide, say, sodium sulphide, acting on a considerable quantity of ferrous and cupric sulphates, does not produce chalcopyrite but only copper sulphide.

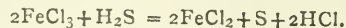
Reducing Action of Sulphides.

Besides taking part in purely metathetic reactions both soluble and insoluble sulphides may act as reducing agents. This action may be referred to the slight electro-affinity of sulphur, which produces the partial reaction:—

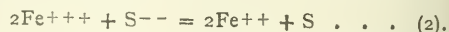


This reaction has a strong tendency to occur whenever it can be linked with a reaction of positive ions yielding

positive electricity. For example, we are familiar with the action of hydrogen sulphide in acid solution on ferric salts:—

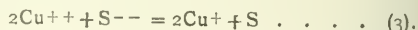


If the reaction is considered to be essentially one between ions we have:—



This reaction shows the neutralisation of the positive and negative charges and the precipitation of free sulphur.

The application of the reducing tendency of sulphide ions here suggested and illustrated should lead to interesting conclusions with other than iron salts. With cupric salts, for example, we should expect that the sulphide ions would tend to reduce cupric ions, along the line of the following equation:—



Data on this possibility are scanty. Several investigators (see Note) have called attention to the fact that hydrogen sulphide produces in a solution of cupric sulphate a precipitate in which there is some free sulphur and a deficit in the amount of combined sulphur required by the formula CuS . According to Schweizer, there is usually about 7·2 per cent cuprous sulphide, Cu_2S —that is, if the complex is interpreted as a mixture of cupric and cuprous sulphide—but, according to the more recent work of Clark, if such a precipitate is filtered off and digested for a long time with a solution of hydrogen sulphide in water the residue after removal of free sulphur contains about 71 per cent cuprous sulphide.

(NOTE.—Julius Thomsen, "Ueber die Zusammensetzung des auf nassem Wege Gebildeten Schwefelkupfers," *Deut. Chem. Gesell. Ber.*, 1878, xi., 2043; A. Ditte, "Action de Sulfure de Cuivre sur le Sulfure de Potassium," *Comptes Rendus*, 1884, xcvi., 1429; Bohuslav Brauner, "Action of Hydrogen Sulphide on Cupric Salt Solutions," *CHEMICAL NEWS*, 1896, lxxiv., 99; E. Schweizer, "Diss. Erlangen," 1908, p. 34; J. D. Clark, "A Chemical Study of the Enrichment of Copper Sulphide Ores," "New Mexico Univ. Diss.," 1914, p. 106).

The study of the ionic reactions suggested by Equation 3 as a possible equilibrium governed by the mass law is rendered difficult by the fact that sulphur and the two sulphides of copper are very insoluble. Of the different concentrations in Equation 3 that of Cu^{++} will be determined by the solubility product of cupric sulphide and that of Cu^{+} by the solubility product of cuprous sulphide. The concentration of free sulphur may presumably be varied from zero to that of a saturated solution of sulphur. The concentration of sulphide ions, S^{--} , may be varied most widely, both by changes in total concentration and by the use of alkaline solutions in which the ionisation of hydrogen sulphide is enormously increased. The use of an alkaline solution also serves to keep the concentration of free sulphur, S, below that of a solution saturated with sulphur on account of the formation of alkali polysulphide.

If we increase the concentration of the sulphide ions, S^{--} , there should be an increase in the cuprous ion concentration, Cu^{+} , if Equation 3 is significant, and presumably more cuprous sulphide might then be precipitated.

A number of experiments were made, directed wholly toward securing a precipitate with a high percentage of cuprous sulphide, especially by the use of alkaline solutions. The results are summarised in the following table. The precipitations were made hot by adding the cupric sulphate to the alkaline sulphide. The precipitate was washed by decantation, finally with alcohol and ether, well pressed between filter-papers, and dried over sulphuric acid.

These results prove that the immediate precipitate produced by alkaline sulphides contains a much higher percentage of cuprous sulphide than that formed by hydrogen sulphide in acid solutions. The results strengthen the supposition that the equilibrium shown in Equation

determines the composition of the precipitate to some extent, since the sulphide ion concentration varies with the alkalinity (Joseph Knox, "A Study of the Sulphur Anion and of Complex Sulphur Anions," *Faraday Soc. Trans.*, 1908, iv., 47). It appeared impossible, however, by this method to obtain a precipitate of pure cuprous sulphide. The experiments of Ditte show that a concentrated solution of potassium sulphide will convert copper entirely into the cuprous state, but he says that a dilute solution is without effect (*Comptes Rendus*, 1884, xcvi., 1429). My experiments seem to modify Ditte's conclusions. The further solution of the problem would seem to require a more careful study of the reversibility of the action with respect to variations in the concentrations of sulphide ions and free sulphur.

The reducing action of sulphide ions on other metallic salt solutions has not been studied.

Action of Alkaline Soluble Sulphide Solutions on Cupric Sulphate.

Experiment.	Grm. equivalents taken per litre of the mixture.			Percentage of Cu_2S in precipitate.
	CuSO_4 .	Na_2S .	NaOH .	
126 ..	0.091	0.091	0.017	18.3
127 ..	0.059	0.112	0.022	31.1
128 ..	0.035	0.069	0.130	47.6
130 ..	0.001	0.002	0.200	55.8
131 ..	0.016	0.155	0.146	61.8
129 ..	0.014	0.028	0.158	69.3
	CuCl_2			
132 ..	0.05	0.10	0.10	49.8

Electric Activity in Sulphides.

Since insoluble metallic sulphides are conductors of electricity the equalisation of chemical differences, especially differences in degree of oxidation, can take place through electric action over appreciable distances. Thus the deposition of such metals as gold, silver, and copper may occur at one end of a conducting filament while the oxidation of a sulphide or any other oxidisable substance is occurring at the other end of the system constituting the metallic portion of the circuit. The associations of products produced in this way will naturally be different from those produced under conditions of thorough admixture. Further, not only will dissimilar sulphides and metals manifest reciprocal influences on each other through electric activity, but effects from active solutions will be transmitted as far as the complete circuits extend. I have discussed these matters elsewhere ("Electric Activity in Ore Deposits," *Bull.* 548, 1914, U.S. Geol. Survey), and need refer to only one phase of the subject further in this connection.

In studying chalcocite enrichment A. C. Spencer has reached the conclusion that the change of pyrite or chalcopyrite to chalcocite may be considered as an alteration involving a series of steps, or perhaps even a continuous progression through indefinite compounds or mixtures of iron-copper sulphides. He succeeded in bringing about the change of chalcopyrite at least into chalcocite through bornite and covellite in several artificial ways. One of these ways consisted in touching the specimens immersed in cupric sulphate by an iron nail. Since there is every reason to believe that the iron affected the sulphides through electric action it seems worth while to quote his account of this experiment as an illustration of possible electric action (A. C. Spencer, "Chalcocite Enrichment," *Econ. Geology*, 1913, viii., 629).

The colours . . . referred to above may be readily obtained by another simple procedure, and the observer can hardly fail to conclude that the colours obtained indicate the formation of the minerals bornite, covellite, and chalcocite. If any member of the series chalcopyrite, bornite, covellite is touched by a piece of iron while it is

immersed in a cupric sulphate solution the mineral changes colour almost instantly, and in a short time becomes coated with the mineral next above it in the series. The brilliant indigo of covellite changes to the dull grey so characteristic of chalcocite, bornite assumes a blue colour unmistakably like that of covellite, and chalcopyrite takes on a bronzy hue resembling that of bornite. Furthermore, within a very short time the bronze plating on chalcopyrite gives place to or is hidden by a film of covellite; then within an hour or so the surface turns to a chalcocite grey, and finally metallic copper is deposited. When pyrite is used in place of a cupriferous sulphide the effect of the iron is sufficient to throw down metallic copper rather quickly, but by scraping away the metal and again placing the mineral in contact with iron in the solution it is possible to obtain deposits of copper sulphides. In this way spots having somewhat the same colour as chalcopyrite and others bronzy like bornite may be developed on pyrite along with unmistakable films of covellite and of chalcocite. If copper is used instead of iron the results are essentially the same with chalcopyrite, bornite, and covellite. For instance, covellite may be coated with chalcocite by contact with copper in a solution of cupric sulphate. It is obvious that the speed of reaction may be varied by employing different metals as inductors, or by employing minerals to cause electrolytic action. Very pleasing results have been obtained by placing in a solution of cupric sulphate a polished specimen of intergrown chalcopyrite and pyrrhotite. Here a pinkish bronze colour resembling that of bornite appeared within a few days, but gradually changed to purple, deep purple, and finally to indigo blue. On the most active grains the covellite colour was fully developed in about eight weeks, but the surface in general became blue only after twelve weeks, and even then certain areas were still bronzy. At the end of four months no grey colour had developed to indicate the formation of chalcocite, but the colour was a paler blue than that of natural covellite.

It may be suggested that the results described, which were obtained under ordinary temperatures, may actually epitomise the course of reaction between the primary sulphides and copper salts held in oxidised solutions penetrating from the surface. Even if the means employed to produce the results in a short time are not comparable with those involved in natural processes, perhaps the conditions under which the experiments were made may be considered to be less unnatural than those prevailing in mineral syntheses effected under high temperatures.

Summary of Results of Experiments with Sulphides.

1. The concentration of the sulphide ion is so greatly affected by change of acidity that this change is the principal factor determining the precipitation of sulphides.
2. The solubility of the several sulphides, however, differs so greatly that complete separations by fractional precipitation are possible; for example, copper from zinc.
3. A mixture of two metallic salts yields, by fractional precipitation, an initial precipitate containing the sulphides of both metals, but as a rule, if the mixture is heated or is permitted to stand, one sulphide largely or wholly re-dissolves.
4. The order of precipitation, beginning with the metal that separates first, is palladium, mercury, silver, copper, bismuth, cadmium, antimony, tin, lead, zinc, nickel, cobalt, ferrous iron, arsenic, thallium, manganese.
5. Attempts to form chalcopyrite by fractional precipitation of ferrous and cupric sulphate were unsuccessful.
6. Soluble sulphides may act as reducing agents. This action affects the composition of precipitates of copper sulphide, and may explain the anomalous position of silver in the precipitation series.
7. At one stage of the action produced by an admixture of sulphides and metallic salts electric activity may determine the products formed.

(To be continued.)

STELLITE.*

By ELWOOD HAYNES.

THE name "Stellite" was coined from the Latin word "stella," a star. This name was first applied to a binary alloy consisting of cobalt and chromium, which the writer discovered and produced as early as 1899. It was not until some years later that its properties were fully investigated, when it was found to possess the following properties:—

1. A considerable amount of hardness, as alloys containing 10 per cent or more of chromium could not be successfully filed, though the file could slowly wear away the surface of the metal.

2. Considerable toughness. Alloys containing as high as 25 per cent chromium, showing elongation of 10 per cent or more.

3. Comparatively high tensile strength and elastic limit. A bar of forged metal showing elastic limit of 85,000 lbs. and tensile strength of 110,000 lbs.

4. Fine colour and lustre. The colour of the alloy lies between that of steel and silver.

5. Absolute resistance to oxidation or other changes when exposed to either dry or moist atmosphere at all temperatures under a dull red heat.

In 1911 the writer succeeded in producing very hard alloys, consisting essentially of cobalt and chromium, by adding tungsten or molybdenum, or both. The hard alloys thus formed could not be scratched with the file, but in turn would scratch any steel that could be produced. Some of these alloys were extremely brittle, and those used for lathe tools require very careful handling. Some of them that showed excellent cutting qualities when used for turning cast iron or steel would break very easily if subjected to any abnormal stress.

In order to determine the stress required to break a $\frac{1}{2}$ inch square tool, for example, a small clamp was made in the form of a slot, precisely similar to the slot used in the tool holder.

A short piece or bar of stellite was placed in this slot and pressure applied vertically near the end of the bar, at a distance of an inch from the clamp. Some of the weaker bars broke at from 100 to 300 lbs. pressure under this test. Gradually the strength of the bars was increased until they would readily withstand 1000 lbs., and at this time bars are produced for turning steel which readily withstand from 1200 to 1500 lbs. under the same test. The very hard bars used for turning cast iron usually stand from 800 to 1200 lbs. under this test. Bars that would stand as high as 1850 lbs. have been produced, but were not found to be equal in cutting qualities to some other compositions of slightly less strength. It should be remarked at this point that the cutting qualities of any steel do not depend primarily upon its strength but upon the suitable combination of strength, hardness, resistance to wear, &c. The strength of a tool is in reality a question of elastic limit. Steels possessing this quality to the highest degree are nickel steels, nickel chrome steels, and vanadium chrome steels. For turning steel and iron, however, they are of little or no value, since they lack in hardness and resistance to abrasion, particularly at high temperature.

The virtue of the stellite tool lies in its ability to maintain its cutting edge at a high rate of speed at temperatures which would immediately cause the failure of any known tools containing any notable quantity of iron. Its great hardness and resistance to abrasion at all working temperatures are likewise valuable properties.

Owing to the fact that stellite retains its hardness even at a full red heat it cannot be forged. This fact, however, is rather a virtue than a detriment so far as use is concerned, because if the alloy would soften sufficiently for

forging when heated it would, of course, immediately lose its cutting edge at the same temperature, and this would limit its usefulness to a marked degree.

From the above fact stellite can only be reduced to the desired form by casting it in dies in the form of bars, which are afterward ground to a cutting edge. Its capabilities as a lathe tool are now universally acknowledged, though in certain cases failures have resulted, due to improper knowledge of the alloy and its peculiarities. It should be remembered that it is *not a steel*, and therefore requires special handling, which enables the operator to utilise its valuable properties to the best advantage.

Without going into the method of handling the alloy some results obtained by its use would perhaps not be out of place. It was recently ascertained that a $\frac{5}{8}$ in. square by $2\frac{1}{2}$ in. long piece of stellite, ground to the form of a grooving tool, cut 14,000 grooves in cast-iron pistons ranging from $3\frac{1}{2}$ in. to $4\frac{1}{4}$ in. in diameter before it became too much worn off for further use. This work was performed in regular practice and not as a test. A still more remarkable and more recent performance has just come to light in the same factory. A stellite tool of the same dimensions as that mentioned above, but which was ground to the round-nose form and used for turning pistons, turned off more than 8000 lbs. of cast-iron before becoming too short for use. Considering only the portion of the tool which was actually ground away, the tool turned off 1000 times its weight of cast-iron before becoming too short for service.

Both of the above tools were made especially for turning cast-iron. Another combination is used for turning steel, which has also shown equally remarkable results. These tools are now being used extensively for turning shrapnel shells at high speed for the European war.

While long wear is an important property in a lathe tool, it is not the essential or most valuable property. The value of the tool, even at the comparatively high price of stellite, sinks into insignificance when compared with the value of the time saved. For example, in the cast-iron performance mentioned above the stellite cost only about 1c. a day, while it effected a net saving of from 2 to 3 dols. per day. In other words, it is the value of the output which counts and not the cost of the tool.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 23, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"On the Main Crests of Ship Waves, and on Waves in Deep Water due to the Motion of Submerged Bodies." By GEORGE GREEN.

The fundamental problem of ship-waves is to determine the wave disturbance produced by an arbitrary pressure system advancing over the free surface. The present paper gives a general method of obtaining the solution of the moving pressure problem in the form of an integral, and proceeds to the evaluation of the integral in some particular cases of ship-waves. The first case dealt with is that of the moving point-pressure. The integrals are evaluated by applying the principle of stationery phase, and results are obtained for the displacements along the lines of cusps in the well-known ship-waves pattern where "infinities" obscure the true result in the solutions usually given.

It is pointed out that this particular problem, and the method adopted for its solution, have each an interesting optical bearing. The optical analogue of the moving

* Paper presented at the Annual Meeting of the American Institute of Metals, September 23 to October 1, 1915, at Atlantic City, N.J. From the *Chemical Engineer*, xlii., No. 4.

point-pressure problem is the problem presented by a plane light impulse incident upon one side of a prism. The method of solution is shown to be equivalent to obtaining the collective effect of the parts of the whole wave-disturbance which obey the law of extreme path of geometrical optics. The disturbance along a line of cusps is shown to correspond with the wave-disturbance along a caustic in any optical problem.

With reference to ship-waves in which the disturbance is due to the motion of submerged bodies, it is shown that the solution of such problems ultimately reduces to the solution of the moving pressure problem already discussed. Complete solutions of two problems are given—for the submerged cylinder and sphere respectively.

"Investigation of Atmospheric Electrical Variations at Sunrise and Sunset." By E. H. NICHOLS.

Observations were made for a period of fifteen minutes before and fifteen minutes after both sunrise and sunset, using the Wilson compensating gold-leaf electroscope for conductivity and earth-air current, and two Ebert electrometers for measuring the positive and negative electric charges.

The results show a decided uniform decrease in the value of the electrical quantities throughout the sunset period, but the solar effect at sunrise is not at all pronounced.

The potential curves for Kew Observatory were analysed for the years 1912 and 1914 for the thirty-minute period at sunrise and sunset, and monthly means obtained for five-minute intervals, these being corrected for diurnal variation. There is a general increase in the potential at both sunrise and sunset, being more noticeable in the winter months, but there is no evidence of any sudden change.

It is possible that the electrical variations observed may be of assistance in elucidating the problems of wireless transmission.

FARADAY SOCIETY.

Ordinary Meeting, March 15, 1916.

METHODS AND APPLIANCES FOR THE ATTAINMENT OF HIGH TEMPERATURES IN THE LABORATORY.

The Seventy-eighth Ordinary Meeting of the Faraday Society was held on Wednesday, March 15, 1916, at the Institution of Electrical Engineers, Victoria Embankment, London, W.C. The meeting was devoted to an Informal Discussion on *"Methods and Appliances for the Attainment of High Temperatures in the Laboratory."* Sir ROBERT HADFIELD, F.R.S., President, was in the chair, and the discussion was opened by Dr. J. A. HARKER, F.R.S., of the National Physical Laboratory.

The PRESIDENT, in introducing the subject under discussion, referred to the difficulties experimenters used to labour under in trying to melt small quantities of metals like steel or copper in the laboratory before modern appliances, such as would be described by Dr. Harker, were devised. He then went on to emphasise the importance of laboratory high-temperature furnaces in connection with the standardisation of pyrometric determinations, and he gave a short historical sketch of developments in pyrometry, beginning with Wedgwood's work in 1782, and referring particularly to the work of Le Chatelier and Osmond in France, and W. Siemens, Roberts-Austen, and Callendar in this country, coming down to the more recent work carried out by some who would take part in the present discussion.

Dr. J. A. HARKER, in opening the discussion, said his object was to draw attention to some of the more difficult points in this subject. He dealt almost exclusively with the carbon resistance furnace. The difficulty with this type of furnace was to obtain carbon of the proper qualities, and it was satisfactory to know that in this country the General Electric Company had a stock of carbon tubes for this purpose. Carbon for electric furnaces had

a very variable specific resistance from one sample to another. Graphite had roughly one-fifth the specific resistance of carbon. It was much more uniform and contained very much less inorganic impurities. It differed chiefly in that its hardness was of quite a different order, and it could be cut on a machine like hard wood. With carbon, on the other hand, the lathe tool lost its edge directly and it was impossible to cut rings or patterns unless the specimen was particularly tractable. The temperature coefficient of carbon was practically nil for the first part of its running up and then became strongly negative. Provision had to be made for the fact that the voltage had a tendency to fall rather than rise and the current consequently to go up. For certain purposes when using graphite it was better not to make a plain, straight conductor, but to make it into a spiral or zigzag. One of the difficulties was that at high temperature a neck was likely to form just inside the clamps and irregularities of heating took place, which resulted in a poor life, and there was a great tendency for the whole thing to break in cooling off. Provision had also to be made for the carbon monoxide formed in the furnace to be quickly burnt. The material of which most tubes were made contained inorganic matter up to about 2½ per cent, whilst a thoroughly good specimen contained about ½ per cent. This could nearly all be burnt out by heating quickly to 1800° or 1900°. The need for completely enclosing the carbon furnace was very great, and at the National Physical Laboratory some years ago Mr. Eden built the walls of such a furnace of reinforced concrete, which was considerably better than bricks for preventing the carbon monoxide from getting into the atmosphere. At the same time for laboratory purposes it was essential to have an apparatus of not quite so permanent a character, and in this connection he exhibited a new form of furnace which Mr. Eden had made. The difference between a good and bad type of furnace was all in the small details. In the carbon tube furnace, for instance, it was not at all easy to keep the thing working properly unless the ends were water-cooled. No conductor having a large current density with a big temperature gradient could go on working very long and maintain steady conditions. Sooner or later it caused a big increase in the voltage drop where the copper conductor joined on to the ends, and trouble followed, such as great local heating at the contact. In this new furnace water-cooling had been applied not only to the electrodes but also to the ends, because the furnace was enclosed in an aluminium bomb arrangement, and the ends, which were bolted on to the bomb, were fastened by a packing ring, which had to be kept cool.

The maintenance of the insulation of the carbon tube was also important. One way was to have another tube round the carbon tube with an air space between, but for high-tension work this was thoroughly bad. He had found the simplest and best thing was to use the grade of lampblack used by paint makers, filling up all the space around the carbon tube for a radial distance of three inches. This had been found to be by far the most satisfactory material for ranges of temperature above 1500° or 1600°.

Another point in connection with the new furnace was the important one of economy. It was necessary to obtain high temperatures with small power, and in order to get over this satisfactorily a small portable transformer had been made which could be used in the laboratory. There were eighty turns of primary made up in the simplest way and three secondary turns capable of being coupled in series or parallel. The primary was split so as to be used at 500 volts and downwards, and currents could be obtained up to about 1000 amps. With the insulating soot which he had mentioned the one kilowatt which was necessary to maintain the temperature of 2000° C. in the furnace only heated the outside wall to something over 100° C., so that there was no need for elaborate precautions.

The PRESIDENT pointed out that one of the furnaces exhibited was to be sent to his works at Sheffield.

Dr. HARKER added that Messrs. Hadfield's were going to do with that furnace just what had been done with it at the National Physical Laboratory, namely, standardise optical pyrometers. At the National Physical Laboratory there was a furnace like the one shown mounted beside a bench, on which all pyrometers for verification were put and slid along, the indications being compared with those of the standard.

Mr. R. S. WHIPPLE dwelt on the difficulties he had experienced with optical pyrometers owing to the fact that many optical materials came from Germany, and that it was difficult to get truly monochromatic glass. With regard to Dr. Harker's furnace, what struck him was the way the temperature could be maintained constant. He described some electric furnaces he had seen in America used for gear-hardening. Thermocouples passed through the furnace on to the work, which was simply brought up to the recalcenscent point, as indicated in a Northrup recording pyrometer, and then taken out and quenched. It was a beautiful technical application of scientific phenomena.

Dr. W. ROSENHAIN, F.R.S., said the problems mentioned by Dr. Harker became more difficult when one dealt with a larger space in which it was desired to melt things. The application of electrical heating for making optical glass was at present under investigation, but he would refer to some general difficulties in the use of high-temperature furnaces. One was the presence of carbon compounds; he wanted a furnace as tractable as Dr. Harker's which would be free from carbon. On a small scale a tungsten wire vacuum furnace was effective, and he had melted pure iron ($1525 \pm 5^\circ \text{C.}$) in such a furnace. But the tungsten became brittle and a fresh winding was necessary for each run. Granular tungsten resistors might be used, and so might a carbon resistance furnace with an inner tube, an indifferent gas between the two and a slightly oxidising gas in the inner space. The drop of volts between metal clamps and electrodes in electric furnaces became serious with large currents. He suggested coating the carbon with copper, aluminium, or iron, as the case might be, by the Schoop spray process, burnishing the coating to give a good metallic contact.

The possibilities of gas furnaces were often overlooked. He described two types which he had found useful—the Ségar furnace and one they had evolved at the National Physical Laboratory. The former, which required a 30-ft. chimney, worked quietly and steadily, but for high temperatures he used a special type of injector burner for use with compressed air at 100 lbs. per square inch, and with this temperatures up to 1800°C. were obtained.

Mr. C. R. DARLING remarked that the furnace first described would be very useful for laboratory purposes for melting small quantities of metals. He pointed out some of the drawbacks of platinum-wound furnaces. In furnaces of Dr. Harker's type he had found magnesia bricks satisfactory for outside lagging. Up to 1000°C. furnaces wound with nickel-chrome wire gave good results. A furnace one foot long using an inch tube consumed only $\frac{1}{2}$ kilowatt.

Mr. H. G. LACELL agreed as to the value of nickel-chrome winding. A kieselguhr tube wound with ribbon of this material could be rigged up in a few minutes. He had given up gas-heating for any temperature below 1000°C.

Mr. H. A. KENT had been using a lime furnace for melting platinum and iridium, working beyond 3000°C. , but he had recently obtained excellent results with a crucible of pure zirconia, using an oxy-hydrogen cyclone burner. He hoped it would be possible to make here pure zirconia in granular form; if so, almost any temperature could be obtained with surface combustion.

Mr. A. J. WEBB said he had obtained good results with the Brayshaw burner, with which he had accidentally melted a large piece of platinum with an air pressure of

only 20 lbs. and the ordinary gas supply. Mr. Kent had introduced a good burner similar to Dr. Rosenhain's, in which gas was blown in at the side.

Mr. S. N. BRAYSHAW said it was possible with his burner to melt small quantities of platinum with 3 lbs. air pressure. Noise was of the essence of a good burner; the gas and air had to be sent into the furnace not only mixed but in a state of violent agitation. The turbulence of the explosive mixture in gas-engine cylinders was a parallel phenomenon. He gave a descriptive sketch of the burner which bore his name.

Dr. H. C. GREENWOOD thought there was nothing better than charcoal for insulating carbon tube furnaces, and he held a brief—for many purposes—for the rougher type of furnace built of bricks and charcoal. He described a simple device for the calibration of pyrometers. With regard to large furnaces, something was wanted between the arc furnace and the steel-melting furnace, and where a completely reducing atmosphere was not required the gas furnace had great possibilities. He had melted 100 lbs. of German silver at 1200° in a resistance furnace with a number of resistors in series.

Mr. F. TWYMAN suggested the use of gelatine screens as a substitute for red glass in optical pyrometers.

Dr. W. ROSENHAIN remarked here that at the National Physical Laboratory they were experimenting with zirconia, and he hoped something would emerge that would be generally available.

The PRESIDENT believed that very high pressure blasts would have a great future. Bessemer had worked on them at one time, and he was glad the idea was being taken up again.

Dr. J. A. HARKER, in reply, said that until they had zirconia tubes alumina could be used as a substitute for carbon where that was unsuitable, but it was more expensive than carbon, and at present it was not gastight. He hoped the lampmakers would make squirted tungsten tubes, as they would be extremely useful. In his carbon-tube furnace, to prevent the soot from falling into the spiral groove it was only necessary to wrap filter-paper round the tube; its ash kept the soot from falling. The present uncertain quality of coal-gas was a difficulty in gas furnaces.

THE INSTITUTION OF MINING AND METALLURGY.

PRESIDENTIAL ADDRESS BY SIR R. A. S. REDMAYNE, K.C.B.

(Continued from p. 155).

British Mineral Resources (continued).

THE Staffordshire Mines Drainage Scheme may not perhaps be an ideal one in practice, and some doubt may be thrown on the findings of the Royal Commission on Coal Supplies in respect thereof, yet there can be no doubt that had not the scheme become operative many mines now being worked would have been abandoned or never opened. The scheme probably could be improved on and extended.

(5) On the Continent the practice of hydraulic stowage of wastes is much in vogue, with consequent greater recovery of coal.

(6) Improvement in mechanical coal cutters. Many seams are at present being worked by mechanical coal cutters, especially thin seams, which would otherwise be left unwrought. It is possible that there is room for improvement in the machinery applied to coal getting, and probable that its use is capable of wider application.

(7) Improved methods of working, viz., of thick seams, may be suggested, in which respect those interested in this matter are referred to the Report of the Expert Committee appointed by the Royal Commission on Mines, on accidents from falls of ground, &c., in which the subject is dealt with.

(8) The Royal Commission on Coal Supplies endorsed the recommendation of the Mining Royalties Commission, that greater facilities should be afforded to tenants for life on settled estates in dealing with mineral property.

(9) Before the abandonment of any mine is permitted plans and conditions might be examined and investigated.

As to the question of waste, how can we, for instance, compel a colliery owner to work and raise to the surface coal which is less profitable than other coal in his mine, even though his not doing so may result in a seam or portion of a seam being irretrievably lost? It is lamentable that such loss should occur. But one means, though a doubtful one, suggests itself for the prevention of this form of loss, viz., the imposition of a fine or tax on lessors of mining property (not the lessee) in respect of all coal (1) worked and left below ground or (2) unworked and abandoned—by abandoned I mean *irretrievably* lost. The lessor would then presumably impose on the lessee or intending lessee of the royalty such terms by way of rent, &c., as to ensure all available coal being got.

As to the uneconomical use of coal, it might naturally be supposed that persons who purchase coal are desirous of making it go as far as possible, i.e., of using it to the best advantage. This to a great extent is true, but, on the other hand, two important factors are largely absent: (1) knowledge as to how to use fuel to the best advantage, and (2) lack of facilities for rendering its economic use possible.

Whether or not the creation of some such organisation as I have mentioned in respect of wastage in the working of our coal supplies is one of practical politics or not is open to doubt, but there can be little difference of opinion as to the advisability and the great advantage resulting from a thorough investigation of the subject of the more economical use of coal as a means of creating power (in steam and internal combustion engines) and for the production of coke and the by-products resulting from the distillation of the coal.

Prof. Bone, in his able and suggestive lecture on "The Utilisation of Energy from Coal," recently delivered before the Royal Institution of Great Britain, has indicated many directions in which greater value might be obtained from the utilisation of our coal resources, and has pointed to the need of systematic research, and I would like to say here that he must have the whole-hearted concurrence of all experts in matters relating to fuel in his statement that "the problem will never be solved from a national standpoint by the policy of leaving it to the slow operation of isolated and independent investigation. What is needed is a patriotic exchange and pooling of experience, a willingness to co-operate wholeheartedly and effectively under skilled guidance and advice for a national benefit, and this cannot be achieved except on the basis of some national organisation." The British Association has lately appointed a strong committee to consider the whole question from a national standpoint, "and to report upon the chief direction in which large economies can be effected and the best means by which the community can exercise their realisation." But it is, I think, a matter for consideration whether work of such national importance, covering so extensive a field, requiring for its successful completion the wholtime service of able chemists and the expenditure of large sums of money, could not be better carried out by a body of a more permanent character than a committee of the British Association. Personally I feel that the State should undertake and finance such an enquiry.

The work could be divided, perhaps, into sections:—(a) Documentation: gathering together and summarising the information available in works, transactions, and periodicals; (b) the carrying out of a chemical survey of the coal deposits of the kingdom seam by seam, and mapping the areas in accordance with quality and chemical characteristics. The information which such a survey would provide would be of the greatest value to consumers

of fuel, and would be preliminary to some extent to (c), the scientific and industrial research relating to the more economical use of coal in the production of energy and its carbonisation and the recovery of by-products.

It will be seen that the work would have to be carried out in the office, the laboratory, and on a large scale in the factory. It would require for its effective consummation the co-operation of the chemist, the mining engineer, the geologist, and the manufacturer.

I think the solution of the problem of the economical consumption of fuel in the production of energy really lies in the more extensive employment of electric motive power—the establishment of large distributing power-stations which use fuel most economically. This is the surest way to secure general economic use of fuel energy.

I have recently discussed the subject of the more economical use of coal with my friend Mr. Merz, who is, as you know, a distinguished electrical engineer well acquainted with Continental and American practice, and would like to place before you a brief summary of the conclusions come to on that occasion:—

(1) *A saving in the consumption of fuel can be made by more scientific use of the fuel.*—It is probably understating the case to say that the present power requirements of the country, speaking of "power" in its broadest sense, could be met by utilising *one-third* of the fuel consumed at present if, instead of the fuel being utilised in small units of machinery, its use were concentrated in large generating centres, where the highest expert skill (chemical and engineering) could be devoted to its proper consumption.

Such a result can only be attained by such centralisation of production and transmission being in the hands of bodies specially constituted for the purpose of generation and transmission of power, as distinct from every user making his own power in his own way.

(2) *There now follows the question, How is it possible to accelerate this development?*—It is necessary to appreciate that the proper development of such a business means spending capital upon which it is probably not possible, however efficiently it is done, to secure a return of more than 1 per cent during the first year, rising by, say, 1 per cent per annum up to a proper return.

The German Government, and particularly the German States, have appreciated this point, and there are now in force in large areas in Germany arrangements by which loans are granted to operating companies, commencing at a very small rate and rising gradually to a reasonable rate of interest.

Something of the kind is certainly necessary in this country if a more rapid rate of progress is to be attained, the rate of progress now being much curtailed by the difficulty of financing.

On the question of financing such undertakings, this could be done by the State or by a modification of the present system of banking. In either case it should be remembered that the amount of capital involved in dealing as suggested with the problem, with a view to accelerating progress, is not really large: £2,000,000 or £3,000,000 a year for ten years, properly spent, would go a very long way to starting things on right lines, and in five years' time the State, if it were the financing agent, would be getting a very satisfactory revenue in the shape of rentals.

The need in Great Britain for the "financial organisation of enterprise" is very great. The part played by the banks in Germany in the past in assisting enterprise is described in the following letter from a British engineering manufacturer, quoted in a recent issue of the Engineering Supplement of the *Times*. The writer says:—

"It will be necessary to arrange that practical assistance is always available for promising developments. The great strength of the electrical engineering industry in Germany is not due to superior technical qualifications, . . . but to the systematic financial aid which has enabled them to meet all demands as they arose, while giving the

easiest possible terms to their foreign clients. The banks here have almost entirely confined themselves to the mechanical transfer of credit and the negotiation of the instruments of credit with an efficiency of very high order, and it may be that it is desirable to keep this business separate and distinct from the financing of enterprise. For the latter we require to organise the 'possessors of credit' and link them with the 'possessors of enterprise' through an organised body of experts possessing specialised technical and commercial knowledge, imagination, and sound judgment, who can pronounce of the soundness of any scheme submitted and the proposals for its execution."

In this connection one welcomes the statement of the President of the Board of Trade in the speech already referred to. Speaking of banks and banking Mr. Runciman said:—

"I agree . . . that the extension of commercial banking, as distinct from the more conservative form of banking which is our custom in this country, might be fostered here. . . . If we are to do more in the future our banks must be a little more adventurous. If they cannot, in consonance with their present system, be more adventurous, let us have some additional institutions; at all events commercial banking must play a large part if we are to hold our own against Germany."

The probability—or at any rate the possibility—presents itself of the Government having to give financial assistance to industry after the war. The erection of buildings and the formation of roads, to give possible instances, would not constitute financially remunerative undertakings; that is to say, the State would not receive a monetary return on the capital expended thereon, whereas were funds allocated to the extension of electrical enterprise on the lines indicated an increasing income, amounting finally to a handsome return, would accrue to the State. There should be no difficulty, therefore, in the way of financial assistance being forthcoming, for, granted a fair return on the money it expends, the credit of the State is unlimited. The enormous income, amounting to many millions per annum, derivable from the increased quantity of coal available for export, is an obvious factor in the case.

(3) *Could matters be accelerated by legislation?*—The answer is, "Yes." Even if something were done as suggested above, it would also be necessary to have more active co-operation between municipalities and companies operating in adjacent territories. The old idea that electric power must be all sold by a municipality or all sold by a company is disappearing, and the time appears ripe for a scheme entailing some closer co-operation between municipalities and companies. But some "lead" would have to be given by the Government and further legislation would be necessary. The slow progress up to date is a proof that the business cannot be entirely dealt with by municipalities, though they can do a great deal.

In considering these points it should not be forgotten that the United Kingdom, on account of the density of its population compared with other countries and the comparatively small distance between industrial centres, is far more suitable to a general use of electricity for power purposes than any other country, including Germany, and far more suitable than the United States of America.

It is due to the want of realisation of the two points mentioned above that this country, instead of being ahead of both the United States and Germany in such a development, is behind except in one or two instances.

(b) *Our Resources of Iron Ore and Limestone.*

Second only in importance to our coal supplies are our stores of iron ore. The information at our disposal respecting the extent and value of our home supplies of all classes of iron ore is indefinite and incomplete, which is the more regrettable seeing that the exhaustion of the better sorts of ironstone is proceeding at a great rate, and their complete exhaustion is much nearer than that of our coal supplies.

We have extensive deposits of stratified low-grade ironstones, in respect of some of which our knowledge is extensive, but as to others we have very meagre information.

Normally the greater part of the iron ore smelted in the United Kingdom is imported from the Continent of Europe, largely owing to the fact that we are unable to produce a sufficient quantity of high-grade ore—though the red hematite of Cumberland and Lancashire is an ore of exceptional purity it is limited in quantity—there are only forty-five mines working it, raising 1,630,664 tons per annum. Is it too much to hope that a method will be devised for the more economic reduction of our low-grade ores and the conversion of the pig into high-class steel? The "basic" process of making steel requires, of course, for its economic success that the iron is sufficiently high in phosphorus. "In some cases commercial results might be obtained by mixing ores with a high phosphorus content with ores less rich in phosphorus, but unless some method can be discovered by which phosphatic substances can be economically added the great bulk of the iron ore resources of this country, which lie in conjunction with the coal measures, cannot be converted into steel with profit. This appears to offer a great opportunity for scientific research" (Engineering Supplement of the *Times*, January 28, 1916). It will be seen that there is room for a chemical survey of our ironstone deposits as well as of our coal seams. The value of applying such a survey to our limestones also will appear evident. To give one instance: in the "basic" process of making steel only the purest lime can be employed for the "basic" lining of the "converter."

Were a chemical survey and geological inventory of our coal, iron ore, and limestone resources available, it would be possible to determine readily the geographical position of relatively suitable products for the different industrial processes connected with these substances. Such a survey might be extended to cover the clays of the country also, and possibly the sands in connection with the question of glass making.

I have dealt at some length with the subject of fuel, and have touched on that of iron also, as they are matters of such general interest to all mining men, but I realise that they are subjects which come more particularly within the purview of our sister society, the Institution of Mining Engineers, which institution, I doubt not, is giving much thought to the problems I have to-day brought forward.

(c) *Our Resources of Non-ferrous Metals.*

Allusion has been made to the vast and varied mineral resources of the British Empire. It has been pointed out that nearly every conceivable ore, stone, or clay can be found in quantity within the bounds of that empire. The natural inference is that advantage would result to the Government were it to make use of the organised bodies of mining and metallurgical engineers established in this country for the purpose of reference and advice on matters pertaining to those resources. I think the idea is a natural corollary to that part of Mr. Runciman's speech relating to metals.

But passing to a consideration of the smaller part of the subject, what is the position in respect of the non-ferrous metals within the United Kingdom itself? One is glad to see that three volumes of "Special Reports on the Mineral Resources of Great Britain," dealing with the use, distribution, and treatment of ores of various metals, prepared by the Director of the Geological Survey, have recently been issued in response to numerous enquiries that have arisen through the conditions brought about by the war. Vol. I. treats of tungsten and manganese ores, Vol. II. of barytes and witherite, and Vol. III. of gypsum, anhydrite, celestine, and strontianite. We may hope and expect that the series will be still further projected to include all the ores mined or occurring in the United Kingdom.

At one time we derived much larger supplies of copper and lead from our home resources than at present. A com-

parative statement for the years 1848, 1857, 1873, 1882, 1913, and 1914 (given in an appendix to Address), illustrate the falling-off in output from British mines of the ores of these metals, and shows also the comparative outputs in respect of tin, zinc, barium, manganese, and tungsten for the same periods, as well as the amounts imported of all the ores or metals named. The imports are on a vastly increasing scale. The waning outputs in respect of lead ore, at any rate, and the comparatively small outputs in respect of the other ores named, with the possible exception of copper, are due not to the proximate exhaustion of the deposits but largely to the discovery of more extensive, richer, or more cheaply worked deposits in some of the colonies and foreign countries. Against such factors there is of course no contending, but some doubt may be felt as to whether we have done all that is possible and practicable to further develop our home resources, especially of tin, lead, and zinc. We cannot shut our eyes to the fact that there are mines being successfully worked abroad which do not present more favourable features than such as characterise some of our long-abandoned mines. I have often thought, for instance, that in view of the great improvements in winding and pumping machinery and in the methods of dressing the ores that have occurred since extensive mining operations ceased in the district that the lead and zinc deposits of Cumberland, known to be considerable, might receive and repay renewed attention.

Our supplies of manganese ore are very small, and as long as large supplies of far richer ore can be obtained from Russia, India, and Brazil, it is unlikely that the deposits in Carnarvonshire and Merionethshire will be extensively worked.

The value of tungsten in hardening steel is well known. When from 8 to 9 per cent of tungsten is present in tool steel it renders it hard enough to turn chilled rolls. In view of the value and use of this mineral it seems almost incredible, but it is none the less a fact, that before the war the wolfram mined and dressed in Cornwall was sent to Germany, where the tungstic acid was extracted, and re-exported to Sheffield at enhanced prices.

(To be continued).

CORRESPONDENCE.

SULPHATE OF AMMONIA ASSOCIATION.

To the Editor of the Chemical News.

SIR,—We have pleasure in enclosing copies of correspondence which has passed between ourselves and the Board of Agriculture with reference to the question of export licences for sulphate of ammonia.—I am, &c.,

D. MILNE WATSON, Chairman.

84, Horseferry Road, Westminster, March 30, 1916.

Fertilisers Committee,
3, St. James's Square, London, S.W.,
March 30, 1916.

SIR,—I am directed by the Fertilisers Committee of the Board of Agriculture and Fisheries to refer to Mr. Milne Watson's letter of the 23rd inst., and to say that they are glad to learn that your Committee have decided to recommend all manufacturers of sulphate of ammonia not to ask higher prices during April and May than £16 15s. per ton to farmers and £16 5s. per ton to merchants, bags free, f.o.r. at works.

I am to inform you that, with a view to relieving the congestion in the storage accommodation of the various producers, all applications for licences to export to France have now been allowed, and it is proposed to recommence the consideration of applications for export

to any approved destination and consignee as from the 1st prox.—Yours faithfully,

(Signed) H. B. HOUSEMAN
(for H. CHAMBERS, Secretary).

March 23, 1916.

The Right Hon. F. D. ACLAND, M.P.,
Board of Agriculture and Fisheries,
3, St. James's Square, S.W.

DEAR SIR,—In reply to your letter of the 22nd inst., the question of the price at which sulphate of ammonia for agricultural purposes is to be sold in April and May was considered by my Committee to-day, and it was unanimously decided to recommend all manufacturers of sulphate of ammonia not to ask higher prices for these months than £16 15s. to farmers and £16 5s. per ton to merchants, bags free, f.o.r. at works. Seeing that makers generally have loyally co-operated with us in carrying out our suggestions as regards January, February, and March, we have every reason to think that there will be little difficulty in obtaining a general acceptance of these prices for April and May.

We trust, therefore, that your Committee will see their way to remove the existing restrictions on export without further delay. Even if licences are granted immediately it will be many weeks before any quantity of sulphate can be moved from the works owing to the difficulty of securing freight.—Yours faithfully,

D. MILNE WATSON, Chairman.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 7, February 14, 1916.

Atomic Weight of Bismuth.—Echsner de Coninck and Gérard.—The authors obtained from a special metallurgical laboratory a specimen of bismuth which contained sulphur and arsenic. They purified it by fusing several times with saltpetre and transforming the bismuth into chloride. This was then reduced by hydrogen which had been purified by passing through two solutions of permanganate (one warm), concentrated soda solution, and pure sulphuric acid. The bismuth chloride and the pure bismuth were weighed. If the weights are p and p' respectively the atomic weight is given by the equation
$$\frac{x + 106.5}{x} = \frac{p}{p'}$$
 Four determinations were carried out, and the mean was found to be 208.50, which is the value adopted by the International Commission.

Circulation of Manganese in Natural Waters.—V. Vincent.—Several authors have pointed out that natural waters contain manganese, but the question of the form in which it circulates has not yet been elucidated. From the author's experiments it must be concluded that it is present in the form of bicarbonate like calcium bicarbonate. Its formula would be $(\text{CO}_3)_2\text{MnH}_2$, and it would exist only in solution. When a solution of neutral manganese carbonate is treated with a current of carbon dioxide and is afterwards subjected to a vacuum it loses all its carbon dioxide without becoming turbid. A current of pure air causes no alteration, but if the solution is heated it turns yellowish, and on standing gives a deposit of neutral manganese carbonate. At 12° the solubility of manganese carbonate in a saturated solution of carbonic anhydride expressed as manganese is 0.0625 grm. per litre, which is reduced to 0.0013 by prolonged boiling.

As it is very difficult to expel completely all the carbon dioxide it may be concluded that this manganese corresponds to the residual carbonic acid. The oxides of manganese, when exposed to the action of a saturated solution of carbon dioxide, do not all dissolve to the same extent, the amounts dissolving at 13° (expressed in terms of manganese) being:—

Protoxide	0.0291	grm. per litre.
Sesquioxide	0.0046	" "
Dioxide	0.0015	" "

The solubility depends upon the richness of the solution in carbon dioxide and upon the time. Humus, though rich in manganese, is not a solvent for all the oxides, the sesquioxide and dioxide not being attacked by it. In nature it appears that manganese is dissolved by the carbon dioxide liberated by fermentation in the soil, organic matter contributing to the solution by their decomposition. The fact that the commonest natural form of manganese is the sesquioxide explains the poorness of natural waters in manganese. Mineralised waters are richer, and the use of chemical manures favours the solution.

No. 8, February 21, 1916.

Presence of Reducing Substances other than Invert Sugar in Commercial Sugars.—L. Maquenne.—It is known that raw commercial sugars and even most refined sugars contain small quantities of reducing substances, and *a priori* it might be supposed that these substances consist of invert sugar. While, however, it is certain that invert sugar is present in ordinary sugar it has not been shown that it is not accompanied by other substances which are capable of acting upon cupropotassic liquid, and some observations tend to confirm this view. Thus alcoholic fermentation does not cause the disappearance of all the reducing substances in molasses. The author points out that these reducing principles are present in crystallised and refined sugars in a higher proportion than in the raw products, if this proportion is compared with that of the invert sugar which accompanies them. If it is admitted that they behave towards cupric liquid like saccharose rather than like reducing sugars proper, it would be found that the proportion of them is higher the higher the temperature. This is actually found to be the case, and when the estimation is carried out at 100° and at 65° by the author's method which has previously been described, and has been found to be applicable to the determination of invert sugar added to pure cane-sugar, the numbers obtained at 100° are appreciably higher than those found at 65°. If it is assumed that the greater part of the reduction observed at the low temperature is due to invert sugar the difference between the two determinations may be regarded as giving approximately the amount of secondary reducing substances. The weight of these reducing substances other than invert sugar is greater in sugars which contain much of this latter, but the ratio of these two quantities increases with the purity of the sugar. It appears to be impossible to determine exactly the amount of fermentable reducing sugars present when they are accompanied by secondary reducers, but the low temperature method gives an approximation to the truth, and is to be preferred by any other.

Study of the Volta Effect by Induced Radio-activity—Establishment of Two New Facts.—Ed. Sarasin and Th. Tommasina.—The authors have continued the study of the Volta effect by induced radio-activity, using the apparatus already described by them, with some modifications. They have thus shown that when the electrodes are separated by air containing emanations and the radiations of induced radio-activity, and also when the electrodes (of copper and zinc) are in direct contact with one another, and also in contact with induced radio-activities and under the influence of an electrostatic charge, a current is produced. In the cases studied the current always passed from the zinc, and the radio-active medium behaved exactly like the electrolyte of a battery.

New Thermo-electric Method of Studying the Allotropy of Iron and other Metals.—C. Benedicks.—In a closed circuit composed of a homogeneous metal a change of temperature does not give rise to any electromotive force capable of giving a current. Moreover, if the metal possesses an allotropic point of two phases and one part of the circuit is heated in a stationary manner from that point no electromotive force results; the differences of potential of the two phases are mutually annulled for reasons of symmetry. If, on the other hand, the elevation of temperature is not stationary the two surfaces of contact between the phases may have a slight difference of temperature which may give rise to an electromotive force. Suppose that the heated zone is displaced along the current: the temperature of allotropic transition being always a little higher on heating than on cooling (Osmond), a constant electromotive force will be set up; it will depend upon the direction of displacement, the magnitude of the hysteresis, and the electromotive force between the two phases. Trouton has already shown that a thermo-electric current is produced in an iron wire when it is passed through a gas jet. The author has devised a simple apparatus by which this effect can be measured. The iron wire is passed at a constant velocity (1.6 mm. per second) through a small electric furnace, which is kept at a constant temperature. Measurements are then made of the electromotive forces developed. In this way it was found that iron shows the point A_3 very clearly, but no discontinuity was found for A_2 .

MISCELLANEOUS.

Royal Institution.—A General Meeting of the members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the chair. Mr. John Dewrance, Mr. Samuel Smiles, D.Sc., Mr. Arthur E. Parsons, and Mr. Samuel Nivison were elected Members of the Royal Institution.

Royal Institution.—The Day Lectures after Easter:—Laurence Binyon, two lectures—(1) "Indian and Persian Painting"; (2) "Chinese Painting." Prof. Charles S. Sherrington, two lectures—"Harvey and Pavlov." Thomas Martin Lowy, two lectures—"Optical Research and Chemical Progress." Sir Ray Lankester, three lectures—"Flints and Flint Implements." Sir Alexander C. Mackenzie, three lectures—(1) "The Beginnings of the Orchestra and its Instrumental Combinations"; (2 and 3) "Chamber Music and its Revival in England." Prof. W. H. Bragg, two lectures—"X-Rays and Crystals: (1) New Methods of Research; (2) First Results and their Applications" (the Tyndall Lectures). Prof. H. S. Foxwell, two lectures—"The Finance of the Great War; New Problems and New Solutions; How We Stand To-Day and What Lies Ahead." Prof. Sir James G. Frazer, two lectures—"Folk-Lore in the Old Testament." The Friday evening Discourses will be resumed on May 5. Sir James Mackenzie Davidson, "Electrical Methods in Surgical Advance"; Arthur C. Benson, "Vulgarity"; Colonel Edmond H. Hills, "The Movements of the Earth's Pole"; Prof. Charles G. Barkla, "X-Rays"; Ernest Clarke, "Eyesight and the War."

MEETINGS FOR THE WEEK.

- MONDAY, 10th.—Royal Society of Arts, 4.30. (Fothergill Lecture). "Surveying—Past and Present," by E. A. Reeves.
- TUESDAY, 11th.—Royal Institution, 3. "Modern Horticulture—Old and New Methods of Forcing (the Breaking of Rhythm)," by Prof. F. Keeble.
- Royal Society of Arts, 4.30. "The Forest Resources of Newfoundland," by Sir Daniel Morris.
- THURSDAY, 13th.—Royal Institution, 3. "English Music in the Tudor Period—Songs and Instrumental Pieces," by Dr W. H. Hadow.
- FRIDAY, 14th.—Royal Institution, 5.30. "The Genesis and Absorption of X-rays," by Sir J. J. Thomson.
- SATURDAY, 15th.—Royal Institution, 3. "Radiations from Atoms and Electrons," by Sir J. J. Thomson.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2942.

THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES.*

By ROGER C. WELLS.

(Continued from p. 161).

HYDROXIDES.

Previous Work.

ONLY a few experiments are found in the literature on the fractional precipitation of the common metallic hydroxides. Mills and Smith ("Researches in Chemical Equivalence," *Roy. Soc. Proc.*, 1879, 5th Ser., xxix., 181), in working on nickel and cobalt, found a very narrow margin of difference in precipitability, but this is probably one of the most difficult pairs to separate, although my own experiments indicate that manganese and magnesium are similarly close together. Fink obtained the precipitation series copper, zinc, nickel, cobalt, manganese, and magnesium for the hydroxides of these metals ("Ueber die Affinität der Vitriolmetalle zur Schwefelsäure," *Deut. Chem. Gesell. Ber.*, 1887, xx., 2106). Pickering studied the partial precipitation of copper sulphate solutions only by calcium hydroxide, but this was not strictly a fractionation ("The Chemistry of Bordeaux Mixture," *Chem. Soc. Trans.*, 1907, xci., 1989; 1910, xcvi., 1852).

Solubility of Hydroxides.

The preliminary data available in regard to the solubility of the hydroxides at room temperatures of 20—25°C. are as follows:—

Solubility of Hydroxides.

Grm. equivalents per litre.

Zn(OH) ₂	6.0 × 10 ⁻⁶
Cd(OH) ₂	8.7 × 10 ⁻⁶
Mn(OH) ₂	3.0 × 10 ⁻⁵
Ag ₂ O	4.6 × 10 ⁻⁵
Pb(OH) ₂	9.3 × 10 ⁻⁵
Fe(OH) ₂ (a)	2.7 × 10 ⁻⁵
Mg(OH) ₂	7.5 × 10 ⁻⁴
HgO	2.5 × 10 ⁻⁴
Ca(OH) ₂	4.5 × 10 ⁻²
Sr(OH) ₂	1.3 × 10 ⁻¹
Ba(OH) ₂	4.6 × 10 ⁻¹

(a) A. B. Lamb, "The Potential of Iron Calculated from Equilibrium Measurements," *Am. Chem. Soc. Journ.*, 1910, xxxii., 1218.

Fractional Precipitation of Hydroxides.

By the procedure used in the study of the sulphides the hydroxides of the important metals were fractionally precipitated as follows:—To a dilute solution containing two metallic salts in equivalent quantity, heated nearly to boiling, was added a dilute solution of sodium hydroxide sufficient to precipitate one metal only. The sodium hydroxide contained some barium hydroxide, used to free it from carbonate. Oxidisable salts were precipitated in an atmosphere of hydrogen. The precipitate was kept at a temperature close to 100° for several minutes, and finally filtered off. An aliquot portion of the filtrate was analysed, and the composition of the precipitate was thus determined. In general, one metal was precipitated to a greater extent than the other, and after working out a number of pairs it was found possible to arrange the metals in a series, which may be termed the hydroxide

precipitation series. Although in the experiments with the sulphides the proportions in the precipitate were determined, in nearly every experiment with the hydroxides the results were limited at first to the determination of the order in the series. This order was found to be as follows:—

Order of Solubility of Hydroxides.

- | | |
|-------------------------|--------------------------|
| 1. Ferric hydroxide. | 7. Silver hydroxide. |
| 2. Aluminium hydroxide. | 8. Ferrous hydroxide. |
| 3. Cupric hydroxide. | 9. Manganous hydroxide. |
| 4. Zinc hydroxide. | 10. Magnesium hydroxide. |
| 5. Lead hydroxide. | 11. Calcium hydroxide. |
| 6. Nickelous hydroxide. | |

The pairs determined are shown in the next table.

Pairs of Metals Compared in Fractional Precipitation of Hydroxides.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.
113	Ferric hydroxide	Aluminium
111	"	Copper
112	Aluminium	"
97	Copper	Zinc
98	"	Lead
109	"	Nickel
112	"	Ferrous hydroxide
96	"	Magnesium
100	Zinc	Lead
10	"	Nickel
102	"	Ferrous hydroxide
99	Lead	Silver
	"	Magnesium
106	Nickel	Silver
	"	Ferrous hydroxide
101	Silver	Magnesium
103	Ferrous hydroxide	"
105	"	"
109	Manganese	Calcium
110	Magnesium	"

It will be seen that the precipitation series does not follow the solubility series very closely. Possibly some of the solubility determinations are incorrect, or the matter of hydrolysis may not have been sufficiently considered. However that may be, it is significant that the precipitation series may be correlated with a heat effect, namely, with the heat of reaction—

Sodium hydroxide + metallic sulphate = metallic hydroxide + sodium sulphate.

These heats of reactions are shown in the table below.

Order obtained for the Heat of Reaction of Sodium Hydroxide with Metallic Sulphate.

M.	1.	2.
Hg++	—	11.78
Hg+	—	10.57
Fe+++	10.05	—
Ag	—	8.24
Cr	7.47	—
Cu	6.47	6.25
Al	5.19	—
Pb	—	4.79
Zn	3.99	3.77
Cd	3.59	3.56
Co	3.35	3.13
Fe++	3.23	3.01
Ni	2.64	2.42
Mn	2.45	2.23

1. NaOHAq + M(SO₄)₂Aq = Na(SO₄)₂Aq + MOH.
2. NaOHAq + MnO₃Aq = NaNO₃Aq + MOH.

Although the order here shown does not yet agree exactly with the order obtained in the fractional precipitations the agreement is closer than that between the precipitation series and the order of the solubilities determined directly (see above).

Ferrous and Cupric Hydroxides.

For the purpose of studying one fractionation in greater detail the precipitation of iron and cupric hydroxides was studied over a wide range of concentrations. The fractionations in the table below were carried out with ammonium hydroxide as the precipitant. The results are also plotted in Fig. 2. Dilute solutions were used for these precipitations, the final volume in every experiment being 40 cc. for the quantities stated in the table.

Precipitation of Ferrous and Cupric Sulphate by Ammonium Hydroxide (Mgram. Equivalents).

Cupric sulphate taken.	Ferrous sulphate taken.	Copper in precipitate.	Iron in precipitate.	Colour of precipitate.
0.00	4.00	0.00	2.43	Pale green
0.80	3.20	0.80	1.39	Black
1.10	2.90	1.08	1.01	"
1.50	2.50	1.03	1.07	"
1.70	2.30	1.08	1.05	Brownish
2.00	2.00	1.09	1.07	"
2.50	1.50	1.12	0.97	"
2.85	1.15	1.20	0.95	Orange
2.90	1.10	1.26	0.91	"
3.00	1.00	1.33	0.87	"
3.20	0.80	1.66	0.68	"
4.00	0.00	2.75	0.00	Green

Precipitation of Ferrous and Cupric Sulphate by Sodium Hydroxide (Mgram. Equivalents).

Ferrous sulphate taken in 250 cc. . . .	1.50	4.00	6.20
Cupric sulphate taken in 250 cc. . . .	6.50	4.00	1.80
Iron precipitated by 4 mgram. equivalents of sodium hydroxide. . . .	1.15	1.78	2.03
Copper precipitated.	—	—	1.79

These results show that the copper has a greater tendency to precipitate where equal amounts of both salts are present, and this tendency causes the practical removal of the copper where it is the minor constituent. What looks like evidences of the formation of a molecule, $\text{FeCu}(\text{OH})_4$, may again be due simply to unpreventable oxidation of a portion of the ferrous salt.

Recently, Curtman and St. John have studied the sensitiveness of the hydroxide reactions for the common metals (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1679). They find an order of sensitiveness which differs considerably from the precipitation series here deduced, but it appears that their results are based on optical effects, such as the visibility, colour, and density of the precipitates, so that an exact agreement is not to be expected.

Summary of Results of Experiments with Hydroxides.

1. The precipitation series obtained for the hydroxides, beginning with the most insoluble compound is as follows:

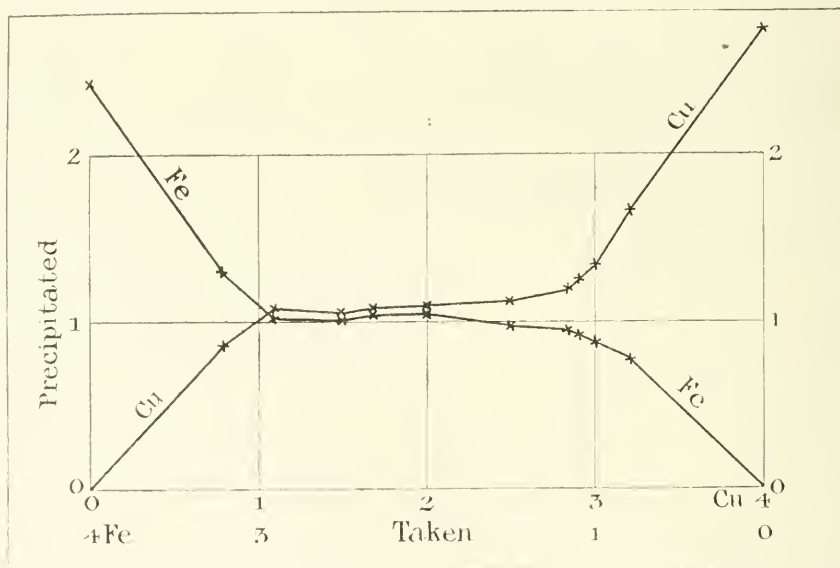


FIG. 2.—Apparently selective precipitation with ferrous and cupric sulphates. The abscissae represent the content of the solution in mgram. equivalents of ferrous and cupric sulphate before the addition of 2 mgram. equivalents of ammonium hydroxide, the ordinates the composition of the resulting precipitate.

These results show a very peculiar selective precipitation. At the extreme concentrations basic salts are precipitated. Although it seemed at first as if the results indicated the formation of a precipitate containing one atom of iron to one of copper, it was afterwards concluded that the oxidation of the ferrous salt had not been wholly prevented, and, in fact, that it could not be wholly prevented on account of the presence of cupric sulphate. As a result of this oxidation ferric hydroxide was precipitated instead of ferrous hydroxide, and therefore the assumption of the formation of a complex compound is unwarranted.

Similarly, solutions of cupric sulphate and ferrous sulphate in varying proportions were precipitated hot out of access of air by sodium hydroxide.

—Ferric hydroxide, aluminium, cupric hydroxide, zinc, lead, nickel, silver, ferrous hydroxide, manganous hydroxide, magnesium, calcium.

2. The series is very nearly the same as that for the heat required for the formation of the hydroxides, namely: —Mercury, ferric hydroxide, silver, copper, aluminium, lead, zinc, cadmium, cobalt, ferrous hydroxide, nickel, manganese.

3. When cupric and ferrous salts are precipitated together by a soluble hydroxide the iron tends to appear as ferric hydroxide, and this fact explains the apparent exceptional precipitation of the two metals together as hydroxides in spite of the fact that cupric hydroxide is more insoluble than ferrous hydroxide.

CARBONATES.

Previous Work.

In 1853 Debus published some quantitative experiments on the fractional precipitation of barium and calcium carbonate ("Ueber Chemische Verwandtschaft," *Liebig's Ann.*, 1853, lxxv., 124). Although some of his conclusions are faulty, an examination of his results shows that calcium competing with barium is precipitated to a greater extent than barium by a soluble carbonate. No other experiments on the fractional precipitation of carbonates have come to my attention except those reported in 1882 by Mills and Bicket ("Researches on Chemical Equivalence," *Phil. Mag.*, 1882, 5th ser., xiii., 169, 177) on the fractional precipitation of nickel and manganese sulphates and nickel and cadmium sulphates by a slight deficiency of sodium carbonate. Their experiments clearly show that cadmium is precipitated to a greater extent than nickel, and that nickel is precipitated to a greater extent than manganese under equal terms of competition. Their experiments were made in the cold, and no time was allowed for any possible readjustment. Other experiments by them on the separate precipitability of these salts show that rather complex precipitates are obtained.

T. Sterry Hunt ("Chemical and Geological Essays," 1878, p. 107) states that a gypsum solution loses no calcium to crystalline dolomite or crystalline carbonate of magnesium, and that even in the presence of carbon dioxide very little magnesium is taken into solution; but with hydrated magnesium carbonate or hydrate of magnesium there is considerably more magnesium dissolved.

To determine the behaviour of certain heavy metals with an excess of carbon dioxide at ordinary temperatures Raikow studied the action of that gas on their hydroxides ("Weitere Untersuchungen über die Einwirkung der Kohlensäure auf die Hydrate der Metalle," *Chem. Zeit.*, 1907, xxxi., 55). He found that basic carbonates were formed with glucinum and yttrium, that acid carbonates were formed with magnesium, thallium, nickel, and cobalt, and slightly with manganese and ferrous iron, and that all the other carbonates were normal. His results do not include any statement of the solubility or insolubility of the carbonates so formed, although they indicate that with an excess of carbon dioxide only silver, cadmium, mercurous, lead, and copper salts among the common elements form insoluble precipitates to any great degree of completeness.

Solubility of Carbonates.

The preliminary data available in regard to the solubility of the carbonates are given in the table (see next column).

The uncertainty of some of these data is illustrated by the figures for silver carbonate, which does not appear in the table. Cox gives 17 parts per million ("Ueber die Löslichkeitsverhältnisse einiger Schwerlöslicher Silbersalze," *Zeit. Phys. Chem.*, 1903, xlv., 11), whereas Moissan gives 30 at 15° C. ("Traité de Chimie Minérale," 1904-1906, v., 580). Moissan states that this is increased to 1040 parts per million when the water is saturated with carbon dioxide. Discrepancies in many of the determinations are probably due to the fact that the acidity of the solutions was not exactly controlled. Even the slight amount of carbon dioxide in the air increases the solubility of carbonates enormously.

Effect of Hydrolysis.

Owing to hydrolysis hydroxides, not carbonates, are precipitated with aluminium, ferric, and chromic salts. "Basic carbonates" are precipitated under ordinary circumstances with zinc, nickel, cobalt, copper, and mercuric salts, and boiling removes the carbon dioxide from these salts to a greater or less extent. When hydrolysis is not so pronounced or the hydroxide is more soluble, normal carbonates are formed as with calcium, manganese, ferrous iron, cadmium, silver, lead, and mercurous salts;

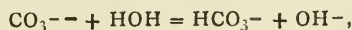
Solubility of Carbonates in Pure Water.

	Temperature. °C.	Grm. equivalents per litre.
PbCO ₃	18	1.6 × 10 ⁻⁵ (a)
FeCO ₃	15	6.2 × 10 ⁻⁵ (b)
ZnCO ₃	15	1.7 × 10 ⁻⁴ (b)
BaCO ₃	16	1.9 × 10 ⁻⁴
CaCO ₃ (calcite)	16	2.6 × 10 ⁻⁴ (c)
CaCO ₃ (aragonite)	15	3.4 × 10 ⁻⁴ (b)
	25	2.86 × 10 ⁻⁴ (d)
	100	3.56 × 10 ⁻⁴ (d)
	15	3.0 × 10 ⁻⁴ (e)
	25	3.06 × 10 ⁻⁴ (d)
	100	3.80 × 10 ⁻⁴ (d)
SrCO ₃	15	3.2 × 10 ⁻⁴ (b)
CoCO ₃	15	4.4 × 10 ⁻⁴ (b)
MnCO ₃	15	4.6 × 10 ⁻⁴ (b)
NiCO ₃	15	4.7 × 10 ⁻⁴ (b)
MgCO ₃	15	2.4 × 10 ⁻³ (b)
Tl ₂ CO ₃	15	1.7 × 10 ⁻¹
Li ₂ CO ₃	15	3.7 × 10 ⁻¹
Na ₂ CO ₃	15	2.6

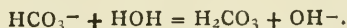
- (a) M. Pleissner, "Ueber die Löslichkeit einiger Bleiverbindungen in Wasser," *Arbeiten aus dem Kaiserl. Gesundheitsamt*, 1907, Bd. 26, Heft 3, Berlin.
(b) J. von Essen, "Recherches Expérimentales sur la Solubilité des Carbonates et des Bicarbonates," Thesis, Geneva, 1897.
(c) T. Schloesing, *Comptes Rendus*, 1872, lxxiv., 1555.
(d) J. Kendall, *Phil. Mag.*, 1912, xxiii., 958.
(e) R. Abegg, "Handbuch der Anorganischen Chemie," 1905, Bd. 2, Abt. 2, p. 157.

these are unchanged on boiling, but the carbonates of lead, mercury, and silver are changed to basic carbonates in time. Lead carbonate suspensions become alkaline at 70° according to Abegg.

For carbonates the chief hydrolytic reaction would be—



and to a less extent—



The degree of hydrolysis of sodium carbonate at 24.1° is shown below for the concentrations stated, the degree expressing the percentage of total sodium present in the form of the hydroxide.

Hydrolysis of Sodium Carbonate at 24.1° C.

Mols. Na ₂ CO ₃ per litre	0.1900	0.0940	0.0477	0.0238
per cent hydrolysis . .	2.12	3.17	4.87	7.10 (a)

- (a) John Shields, "Ueber Hydrolyse in Wässerigen Salzlösungen," *Zeit. Phys. Chem.*, 1893, xii., 167.

The hydrolysis of sodium carbonate may be increased by boiling the solution and the removal of carbon dioxide as follows, starting with a normal solution (F. W. Küster and Max Grütters, "Ueber den Zerfall von Gelöster Soda in Kohlendioxyd und Natriumhydroxyd," *Deut. Chem. Gesell. Ber.*, 1903, xxxvi., 748):—

Hydrolysis of Sodium Carbonate produced by Boiling.

Time of boiling (hours)	1.25	3.5	6.0	8.5	23.3	38.0
Remaining Na ₂ CO ₃ (per cent)	96.7	94.6	92.7	91.4	87.0	83.8
NaOH formed (per cent)	3.3	5.4	7.3	8.6	13.0	17.2

(To be continued).

SELECTING REFRACTORIES FOR THE
FOUNDRY.*By WALTER H. KELLEY,
Harbison-Walker Refractories Company, Pittsburgh.

EVERY superintendent of a foundry insists on knowing the analysis of the coal he is using, while but few investigate the analysis and physical characteristics of their fire brick and fire clay requirements. All fire clay brick are essentially silicates of alumina, and expressed in the lowest terms are composed of the two varieties of clay, namely, the hard, flint or block clay, as it is often termed, which forms the real body of the heat-resisting material, and the soft or plastic clay, acting as a bond to give physical strength to the brick. As conditions may warrant a larger or smaller portion of the hard clay may be calcined previous to its manufacture into brick. Upon the character of these clays, the fineness to which they are ground and the degree of burn given them, depends the character of the brick. In general, a fine ground, hard burned brick gives superior results in the side walls and a more porous, open, and if we may term it, "elastic," brick does better in arch work. There is here given a fairly representative analysis of a high grade Pennsylvania fire clay brick, cited as being merely typical.

	Per cent.
SiO ₂	52.93
Al ₂ O ₃	42.69
Fe ₂ O ₃	1.98
CaO	0.33
MgO	0.38
Alkalis	1.55

It has been demonstrated, other things being equal, that as the percentage of silica increases in a fire brick, the refractoriness decreases, the excess of silica being in a free state and uniting with such impurities as may be present, lowering the fusion point of the brick. The theoretically perfect fire clay, a true silicate of alumina, will show in accordance with the oxygen ratio the following:—Alumina, 53.27 per cent and silica 46.73 per cent. Such a pure silicate of alumina does not, of course, occur in nature, but as a general rule, the nearer the silica and alumina are to these proportions, the more refractory is the material.

Analyses of fire brick taken from various foundries where trouble has been encountered have shown from 59 to 73 per cent of silica, or an even higher percentage. Of the majority of clays used in foundries such analysis indicates that they are made from so-called top vein clays, lying above the coal measures, and such as are more commonly used in the manufacture of sewer pipe, building brick, or fireproof material.

Nevertheless analysis alone does not tell the story as to how any given clay or brick will work out in your furnaces, in the side walls, for instance, where it encounters high temperatures, the scoriifying action of the slag and cinder and the wear and tear of the slice bar or poker. Nor will it tell the results in the arch, often subjected to the most intense heats, with forced or induced draft, with mechanically fired furnaces, and with fuels of various kinds.

The physical structure of the brick should also be considered in making decision as to its selection. Where bituminous coal is used as the fuel, it has been found that a hard dense brick of higher refractoriness gives the best results in the side walls, especially along the clinker line. The importance of using a brick of the proper physical and mechanical composition in side-walls has brought about the introduction of bauxite for this portion of the furnace construction. While they have not as yet probably been given an adequate test, their adoption bids fair to later become a factor in the selection of the material

used in lining at least portions of the several different kinds of furnaces in your equipment. It will be dwelt upon more fully later.

Ordinarily a brick used in the arches should be of not too hard a burn and of a comparatively coarse grind, as a brick of this kind will better withstand the sudden changes of temperature encountered. There are, of course, variations to this rule, as with the use of anthracite coal with blast or forced draft, where the physical structure of the brick should be dense and hard to better withstand the cutting action of the fast-moving gases of combustion.

Care should be exercised in selecting a fire clay for laying up the brick-work of a refractoriness corresponding with the brick. When a manufacturer of a high-grade brick begins to insist that it should be laid up with a clay corresponding in refractoriness his motives are not invariably looked upon as altruistic, but it is a common error to use so low a grade of clay that its plasticity must be reduced by the mixture of sand to give a sufficient sharpness to work the material. In such a case the joints may often melt and run out while the brick themselves would be unaffected. Any addition of lime, mortar, or cement should be avoided, not so much because of the injury done by a very small percentage of this material, as because of the fact that any given percentage is in practical working very often doubled or tripled, due to carelessness in proportioning the mixture.

Air furnaces are particularly severe on fire brick. This is due not so much to the high heats attained as to the intermittent operation of this type of furnace. The highest grade of fire brick obtained is none too good, and care should be exercised in the selection of brick of the proper burn to withstand the variable conditions occurring during the operation of the furnaces.

Hard-burned and fine-ground brick should be used in the side-walls of these furnaces to better withstand the impinging effect of the flames against the walls, deflected, as they are, from the stock which, when originally charged, is very bulky and takes up considerable of the space of the melting zone. Medium-burned and coarse-ground brick should be used in the roofs to overcome spalling and to withstand the variable temperatures naturally occurring.

Considerable of the difficulties with the clinker of the fuel bed adhering to the side-walls of the combustion-chamber have been overcome by the use of a steam-pressed brick along this clinker line. The use of bauxite brick and steam-pressed brick has also overcome to a very considerable extent the scoriifying action of the slag of the bath upon the side-walls of the melting zone.

The side-walls of this type of furnace have to be repaired very often, due to the action of the slag of the bath cutting out the brick-work wherever it touches and thus undermining the upper portion of the walls.

As the temperatures employed in annealing furnaces will vary from only 1000 to 1500° or possibly a little higher, a second quality brick is used almost entirely throughout excepting in furnaces of great width and where the flame of combustion has to carry a considerable distance. Here it has become necessary to use a first quality brick in the fire-boxes of those that are coal fired on account of the higher temperatures necessary to carry the heat across the furnace.

The best practice is to instal the bottom of these furnaces with tile 12 inches in width and 5 inches thick, varying in length from 12 to 18 inches. These tiles are made as tough and dense as it is practicable to make them, so that they will stand the wear and abrasion encountered in the charging of the furnace. As each of these blocks covers a larger area than a standard size 9-inch brick, they afford a more even surface and considerably reduce the number of joints in the brick-work of the bottoms.

In brass-melting furnaces of the pit type wherever a crucible is used and where coke or oil is ordinarily the fuel, a highly refractory brick of medium coarse grind and of a good strong burn give the best results. A brick with these

* From the *Iron Age*: an abstract of a Paper presented September 8 to the American Foundrymen's Association, Chicago.

characteristics will better resist the action of the fused coke and the deposits from the oil.

In the tilting melting type of furnace the most refractory fire-clay brick obtainable is required to secure good results. The brick should be of dense structure and of hard burn to resist the action of the oil and air which are admitted usually under the very heavy pressure. The slags created are very scouring in their action and consequently do not permit of the use of an open or coarse grained brick. Specially shaped brick are usually required to line this type of furnace, to overcome the number of joints occurring when lined with standard brick. A good many of the above furnaces are lined with ganister, which makes a very satisfactory lining material as it can be repaired very handily.

In steel converters the lining most generally used is silica brick, while there are a number lined with ganister, which is a mixture of practically pure silica grits and a refractory clay, which is rammed around wooden forms. Many of these converters are first lined with silica brick, to the surface of which is then added a coating of about 3 inches of ganister. I know of some converter linings thus installed that have given over 18 months' service.

In crucible steel melting furnaces which are usually of the regenerative type, the use of silica brick is rapidly replacing clay brick in the lining of the melting zone. Where formerly there was obtained about four to six months' service with the clay brick-lined furnaces, we have records of furnaces lined with silica brick giving a life of from 36 to 45 months, the average life of these furnaces to-day is from 14 to 18 months.

Brick to be used in cupolas should be dense, hard, tough, and very refractory. Blocks for lining around the bottom of the cupola and for a distance of 4 feet or so above the tuyeres should be made of flint clay high in alumina, with sufficient bond clay to make the brick strong and tough. The manipulation of the clay and the mix, grind, and burn have to be carefully considered to secure the maximum heat resisting capacity, together with ability to stand the cutting action of the blast and the wash of metal and slag. From a distance of about 2 feet above the tuyeres to the charging doors the blocks should be made to withstand abrasion, as well as heat, and they should be exceedingly dense, hard, and strong.

In the electric furnaces silica brick are used entirely, excepting where basic steel is produced; the latter requires that the bottom and side-walls be constructed with magnesia brick to withstand the action of the basic materials charged into furnace. It is surprising how well these brick have withstood the severe treatment given them in this type of furnace. While we all appreciate that silica and magnesia brick will spall severely when subjected to sudden changes of temperatures and fully realising the intermittent operation of these furnaces, still we would not consider any other refractory material than silica or magnesia brick to withstand the high temperatures occurring therein.

The life of the lining of an electric furnace is at the best a very short one, and considerable of the difficulty with the short life of these linings is due to a very considerable extent to the unnecessarily high temperatures often attained. While they have all sorts of devices for registering the voltage and amperes required during the melting of a charge, there is very little attention given to the temperatures attained. In fact, there is no instrument that can be depended upon to record accurately the high temperatures that no doubt are often attained during the operation of the furnaces. I have heard operators of these furnaces state that they judge the working temperature to be slightly over 1900° C. This would mean a temperature of about 120° F. beyond the fusion point of the brick. I have seen the original lining of an electric furnace run for 48 consecutive days and the four or five subsequent linings would last from five to ten days.

Regarding malleable furnaces this practice is about the most severe of any on fire brick. The life of these furnaces is referred to in the number of heats and not days or weeks, and is governed by the service obtained from the brick in the side-walls, as the roof sections or bungs are often renewed during the operation of the furnace.

Fine ground and hard burned brick should be used in that portion of the side-walls as high up as the slag line reaches. Hard burned and highly refractory brick should be used in the balance of the side-walls to resist the impinging effect of the gases of combustion and coarse ground and light burned brick should be used in the bungs to better withstand the variable temperatures naturally occurring in this practice where coal is the fuel most generally used.

A NEW TEST FOR COPPER.*

By W. G. LYLE, L. J. CURTMAN, and J. T. W. MARSHALL.

Introduction.

THE test to be described in this paper is based on the insolubility of the copper salt of α -amino-*n*-caproic acid, $\text{CH}_3(\text{CH}_2)_4\text{CHNH}_2\text{COOH}$. Kudielka in 1903 prepared this acid and its copper, nickel, and cobalt salts, and determined their solubilities in water (*Monatsh.*, 1908, xxix., 351). In the course of their work on the quantitative determination of amino acids Kober and Sugiura state that the insoluble complex which *n*-aminocaproic acid forms with copper may be useful in analytical work (*Journ. Am. Chem. Soc.*, 1913, xxxv., 1584).

Some preliminary work on the part of the authors indicated that an aqueous solution of *n*-aminocaproic acid was an exceedingly valuable reagent for the detection of small amounts of copper. It was the object of this investigation to ascertain the most favourable conditions for the use of this reagent and to determine its applicability to solutions of salts of foreign metals containing small amounts of copper.

The reagent was prepared from commercial *n*-caproic acid by the method proposed by Abderhalden, Fuchs, and Froehlich (*Zeit. Phys. Chem.*, 1913, lxxxvi., 455), and further purified through its copper salt. The solution used throughout our work was prepared by dissolving 0.67 grm. of the acid in 100 cc. of water; the mixture was heated to facilitate solution and then filtered.

It was found that the precipitation of copper by amino-caproic acid was influenced considerably by the presence of free mineral acid. Since mineral acid is liberated as a by-product of the reaction it was decided to employ a buffer in making the test. For this purpose a 40 per cent solution of sodium acetate was found satisfactory.

TABLE I.

Total vol., 3 cc.; 1 cc. of 40 per cent $\text{NaC}_2\text{H}_3\text{O}_2$;
1 cc. of reagent.

No.	Mgrm. Cu.	Result.
1.	1.000	Immediate greyish blue precipitate.
2.	0.500	" " "
3.	0.010	Slight white precipitate.
4.	0.005	Faint precipitate at end of 5 minutes.
5.	0.001	Fair test in 5 minutes; much better in 12 minutes.
6.	0.003	Faint test in 5 minutes; (limit) much better in 12 minutes.
7.	0.002	Negative test in 5 minutes; faintly positive in 12 minutes.
8.	0.001	Negative test in 12 minutes.
9.	0.000	" " " "

* *Journal of the American Chemical Society*, xxxvii., No. 6.

The pure copper salt of *n*-aminocaproic acid was prepared. Evaporation of 1000 cc. portions of an aqueous solution of this compound gave residues from which the solubility of the salt at 18° was calculated to be of the order of 1 in 100,000 (Kudeilka, *loc. cit.*, found the solubility of the copper salt to be 3.6 parts in 100,000 at 23°).

Determination of the Sensitiveness of the Test.—By means of a graduated pipette definite amounts of a standard copper nitrate solution were introduced into a series of test tubes. 1 cc. of 40 per cent sodium acetate and 1 cc. of aminocaproic acid solution were then added, the contents of the tubes shaken and allowed to stand. The results obtained are shown in Table I.

Comments.—The above experiments were repeated a number of times with the same results. The limit of the test in five minutes (0.003 mgrm. Cu in 1 cc. of the original solution) represents a concentration of 1 part in 333,000. While it requires some practice to recognise the test given by 0.003 mgrm. of copper, decided and unmistakable results are obtained with 0.004 mgrm. The precipitate has a tendency to agglutinate, to rise to the surface of the liquid and to creep up the walls of the tube when the latter is gently shaken. This characteristic property of crawling up the sides of the containing vessel makes possible the recognition of smaller amounts of precipitate than would be the case if the precipitate remained in suspension or settled to the bottom of the container. The "crawl" is best seen by gently shaking the tube and viewing it in good light against a dark background. In some of the preliminary tests with 0.004 mgrm. Cu negative results were obtained. An examination into the causes showed that the greasy condition of the tubes prevented the precipitate from crawling; it is therefore imperative in making the test to have the tubes scrupulously clean. This was accomplished by first scrubbing with soap solution, rinsing, then treating with hot chromic acid mixture, and finally rinsing a number of times with distilled water. The solutions to be tested for copper were always carefully examined for any particles in suspension that might be taken for a positive test, and if not absolutely clear the solution was filtered before adding the reagent.

A comparison of the sensitivity towards copper of *n*-aminocaproic acid and synthetic leucine was then made. A solution of Kahlbaum's synthetic leucine of the same strength as our reagent (0.67 per cent) failed to give a precipitate with amounts of copper smaller than 0.03 mgrm. Thus the normal acid will detect about one-tenth the quantity of copper that can be recognised with the iso-derivative. The presence of moderate amounts of the iso-derivative was found to materially diminish the sensitivity of the reagent.

Behaviour of the Reagent with Other Metals.—Having determined the limit of the test in solutions containing copper alone our next step was to ascertain whether there were any other metals which would give the test. To this end 1 cc. of a solution containing 100 mgrms. of the metal as nitrate or chloride was treated with 1 cc. of 40 per cent sodium acetate solution and 1 cc. of aminocaproic acid. Of all the common metals zinc and mercury alone gave precipitates. The test given by zinc under these conditions was very faint, but by diminishing the quantity of zinc to a few milligrams, surprisingly strong reactions were obtained.

This anomalous behaviour of zinc salts necessitated a repetition of the above experiments with small quantities (1–10 mgrm.) of each of the metals. The results showed that mercury and zinc alone gave precipitates and therefore interfere with the test for copper. Methods for overcoming these interferences were devised, and will be given later when these metals are considered.

Whether or not the presence of large amounts of foreign metals would interfere with the detection of relatively minute quantities of copper was the next point investigated. The general procedure was as follows:—

To 1 cc. of the solution containing 100 mgrms. of the foreign metal 0.1 cc. of copper nitrate solution, containing

0.01 mgrm. of Cu, was added. (Because of the relatively small solubility of AlCl_3 2 cc. of solution were required to supply 100 mgrms. of Al.) To this mixture 1 cc. of 40 per cent sodium acetate and 1 cc. of aminocaproic acid were added. A control was run at the same time, and in every case the results were checked by repeating the experiment. Following this procedure good tests were obtained in the presence of Pb, Cd, Ni, Co, Mn, Ba, Sr, Ca, and Mg respectively. With lead solutions a finely divided precipitate appeared in the controls at the end of ten minutes, though they were perfectly clear at the end of five minutes. For this reason it was decided to remove the greater part of the lead with 1 cc. of 20 per cent NaCl solution. After washing the precipitated lead chloride with 1 cc. of cold water good tests and perfect controls were obtained.

Interferences.—It was thought that substances which form only slightly ionisable complexes with copper would interfere with its precipitation by aminocaproic acid. Experiments showed that an excess of KCN inhibits the test. In Table II. the influence of ammonium salts is shown.

TABLE II.

Total volume, 3 cc.; 1 cc. of 40 per cent $\text{NaC}_2\text{H}_3\text{O}_2$;
1 cc. of the reagent.

No.	Mg. Cu.	Result.
1, 2.	0.004 0.6 cc. 50 p.c. NH_4NO_3	Negative in 10 hrs.
3, 4.	0.004 0.6 cc. 30 p.c. NH_4Cl	" "
5, 6.	0.004	Good test in 5 min.

Smaller amounts of ammonium salts were found to retard the formation of a precipitate. Substances containing amino groups were also found to interfere. Thus negative tests for 0.001 mgrm. Cu were obtained in the presence of 10 mgrms. of each of the following substances:—Glycocoll, synthetic leucine, glycyl glycine, "Seiden peptone," and casein.

Sodium citrate was also found to interfere, but, contrary to expectations, good tests were obtained with 0.004 mgrm. Cu in the presence of relatively large amounts of tartrates.

The interference due to ammonium salts and organic matter may readily be removed by ignition.

Special Procedures.

Silver.—The addition of 1 cc. 40 per cent sodium acetate solution to 1 cc. of a 10 per cent Ag solution causes the precipitation of silver acetate. In the absence of sodium acetate a test was not obtained with 0.01 mgrm. Cu in the presence of 1 cc. of 10 per cent silver solution. It was therefore necessary to remove the silver before the test could be applied. This was accomplished by means of sodium chloride. The results of the experiments appear in Table III.

TABLE III.

Total volume before precipitating with 1 cc. 20 per cent NaCl, 1.1 cc. To filtrate added 1 cc. 40 per cent $\text{NaC}_2\text{H}_3\text{O}_2$, 1 cc. reagent.

No.	Mgrm. Ag.	Cu.	Result.
1, 2.	100	0.00	Negative.
3, 4.	100	0.01	Good.

Bismuth.—A solution of $\text{Bi}(\text{NO}_3)_3$ in 10 per cent concentrated HNO_3 , containing 100 mgrms. of the metal per cc., was used. 1 cc. of this solution was found to be too acid to yield a precipitate in the presence of copper. The procedure which gave satisfactory results was as follows:—

To 1 cc. of the bismuth solution 0.01 mgrm. of copper was added. The solution was then diluted to 20 cc. This caused a separation of basic salt. After standing for several minutes 2 cc. NH_4OH (1:1) were added drop by drop and the mixture was filtered. The filtrate and washings were evaporated to a few drops (by removing the ammonium salts at this point better results may be

obtained), taken up with water, filtered again through a very small filter, and then treated with 1 cc. of sodium acetate and 1 cc. of the reagent. Good results were obtained in five minutes.

Antimony.—A 10 per cent solution of antimony as chloride was used. The method employed was similar to that described for bismuth. Good tests and controls were obtained.

Tin.—A solution of SnCl_4 , containing 100 mgrms. Sn in 1 cc., was employed in all our tests with this metal. 1 cc. of this solution yields a precipitate when treated with 1 cc. of 40 per cent sodium acetate. By precipitating the tin with NH_4OH or 40 per cent $\text{NaC}_2\text{H}_3\text{O}_2$ nearly all the copper originally added either combined with or was adsorbed by the precipitate. This was shown by the blue colour of the precipitate. We were unable, moreover, after repeatedly washing the precipitate with either water or dilute NH_4OH to get a test for copper in the combined filtrate and washings after concentration to 0.5 cc. when less than 0.1 mgrm. of Cu was originally present. By removing the ammonium salts from the filtrate the test was rendered more delicate, but 0.02 mgrm. of copper always escaped detection. As nickel does not interfere with the test it was thought that by adding a small amount of this metal (2–10 mgrms.) to the solution of copper and tin it would be possible by means of an excess of potassium hydroxide to precipitate the copper with the nickel and thus keep all the tin in solution. This procedure, however, failed to detect 0.05 mgrm. of copper, for the reason that the precipitated nickel adsorbed some tin which could not be washed out and which interfered with the final test. Based on the volatility of stannic chloride in hydrochloric acid solution, a method was found which yielded uniformly satisfactory results. The solution containing the tin and copper was treated with HCl and evaporated just to dryness; more HCl was then added and the solution again evaporated. After the third evaporation 1 cc. of water was added and the solution treated with 1 cc. of 40 per cent $\text{NaC}_2\text{H}_3\text{O}_2$ and 1 cc. of the reagent. The results are shown in Table IV.

TABLE IV.

No.	Mgrm. Sn.	Mgrm. Cu.	Result.
1.	100	0.100	Strong test.
2.	100	0.010	Strong test.
3.	100	0.006	Good.
4, 5.	100	0.000	Negative.

(To be continued).

SULPHATE OF AMMONIA ASSOCIATION.

Nitre Cake as a Substitute for Sulphuric Acid in the Manufacture of Sulphate of Ammonia.

The Ministry of Munitions recently issued a memorandum with regard to this question, which has met with somewhat severe criticism.

After carefully examining the proposal we feel unable to endorse the recommendation of the Ministry in its original form, but at the same time we are convinced that supplies of sulphuric acid available for industrial purposes will progressively diminish for a considerable time to come.

That being the case, it is both to national and to private interests that all possible economy should be effected in the use of acid as such.

We therefore feel it necessary to recommend makers of sulphate of ammonia to use nitre cake in substitution to the extent and subject to the considerations mentioned below.

Seeing that we have recently been appealing to manufacturers to make sulphate of ammonia testing 25 per cent, it will be readily understood that it is with the greatest reluctance that we feel compelled to issue these suggestions, which will involve the reduction of the percentage of ammonia to 24 per cent, and possibly less.

We therefore wish to make it quite clear that we only advocate the use of nitre cake as a temporary expedient for the duration of the war.

Our recommendations are based on the practical experience gained at a large works which used nitre cake on a working scale over a considerable period. It will be seen that there are dangers to be guarded against, which are not apparent in mere theoretical or laboratory work.

The average composition of the salt produced at the works in question was:—

Ammonia	24.01 per cent.
Free acid	0.88 "
Moisture	2.70 "
Na_2SO_4	3.20 "

corresponding to a consumption of over 7 per cent of nitre cake, equal to about $2\frac{1}{2}$ per cent of acid saved.

Disposal.—We do not recommend any attempt to produce a salt testing less than 24 per cent ammonia unless special forward contracts can be made with manure mixers for lower qualities. Seeing that the lower the content of ammonia the higher will be the percentages of moisture and free acid, thus rendering transport difficult, works contracting with manure mixers should be situated as near to the latter as possible.

Supplies.—The principal supplies of nitre cake are situated in the counties or districts of London, Durham, Cumberland, North and South Wales, Glasgow and Edinburgh, Birmingham, Cornwall, Derby, and Hants. Owing to the extent to which other industries, notably the woollen industry, are using nitre cake, care should be taken to ascertain the probability of supplies being available in given districts.

Nitric Acid Danger.

There are two sources of nitre cake: (1) from sulphuric acid plants, (2) from nitric acid plants. The nitre cake from the first source usually contains 20–35 per cent of free sulphuric acid with traces of nitric acid, and from the second source 30–40 per cent free sulphuric acid and up to 2 per cent or even more of nitric acid.

The presence of free nitric acid causes serious damage to the lead work of the saturator and ultimately destruction of ammonia, and too much care cannot be taken in guarding against the presence of this substance. The danger is emphasised at the present time when nitric acid plants are very hard pressed and it is not profitable to the nitric acid manufacturer to remove the last 1 or 2 per cent of nitric acid from the nitre cake.

The maximum percentage of nitric acid in the nitre cake used by sulphate of ammonia makers should be 0.05 per cent.

Quantity of Nitre Cake to Use.

We do not recommend the use of a quantity of nitre cake exceeding 10 per cent by weight of the acid except in special circumstances.

The nitre cake should be dissolved in water until the solution shows 100 Tw. at 200° F.

Mother liquor from the saturator may also be used for dissolving the nitre cake. This solution must be run into the saturator as hot as possible, and continuously with the acid. The best working strength is 80 to 84 Tw., and the salt produced will vary from 23 to 24 per cent ammonia.

With the solution of nitre cake in water of the strength mentioned above one volume of solution should be used with every ten volumes of 70 per cent chamber acid or its equivalent.

Difficulties if Larger Quantity of Nitre Cake Used.

The difficulties encountered when using large quantities of nitre cake are as follows:—

1. Precipitation of sulphate of soda on adding the nitre cake to the saturator. This causes the production of an irregular quality of salt containing anything down to 15 per cent ammonia.

2. Irregular working of the bath owing to the impossibility of control without frequent titration. The latter is not possible at the present time. The salt produced often contains 2 per cent of acid after leaving the centrifugal machine, and in this case moisture is absorbed in store, and it is not possible to pack the product in bags.

When the quantity of nitre cake used is less than 10 per cent by weight of the acid these difficulties are partially overcome.

The Sulphate of Ammonia Association are prepared to supply lists of nitre cake makers on application.

INTERNATIONAL INSTITUTE OF AGRICULTURE.

INTERNATIONAL CROP REPORT AND AGRICULTURAL STATISTICS.

THE March issue of the *Statistics* published by the International Institute of Agriculture contains information on the areas sown and crop conditions in the Northern Hemisphere and on the harvests in course or lately finished in the Southern Hemisphere.

As regards 1915-16 winter cereal crops in the Northern Hemisphere the new and more important data in the present *Bulletin* include the area sown with wheat in Roumania (1,967,702 hectares, or 101.2 per cent of the corresponding area last year and 106.2 per cent of the quinquennial average 1909-13). The other data on areas seeded published in the preceding *Bulletin* are not modified notably. Crop conditions are generally good in Spain, Italy, Luxemburg, India, and Tunis; growth is delayed in France and Great Britain in consequence of unfavourable weather conditions during February.

The 1915 production data for rice in Egypt being now known (5,918,040 quintals, or 993.0 per cent of the 1914 crop, which was exceptionally scarce), a table is given with data on this crop in Northern Hemisphere countries. For the following group of countries the production of rough rice in 1915 amounts to 634,973,227 quintals, against 541,586,846 in 1914, or 117.2 per cent:—Spain, Italy, United States, India, Japan, and Egypt.

Among the 1915-16 crop data in the Southern Hemisphere are those from the second estimate of production in Argentina:—Wheat 46,988,000 quintals, or 102.5 per cent of the 1914-15 crop and 116 per cent of the 1909-10 to 1913-14 quinquennial average (first estimate = 50,120,000 quintals); oats 10,927,000 quintals, or 131.5 per cent and 134.6 per cent of last year's crop and of the above-mentioned average respectively (first estimate = 10,950,000 quintals); linseed 9,974,000 quintals, or 88.6 per cent of the 1914-15 crop and 124.4 per cent of the above average (first estimate = 10,230,000 quintals). The wheat crop in Uruguay is estimated at 3,000,000 quintals, or 322.6 per cent of last year's.

An Iron-Boron-Carbon-Copper Alloy.—A patent issued recently to Edward D. Gleason, Brooklyn, N.Y., and assigned to the Neu-Metals and Process Co., Long Island City, N.Y., covers an alloy that is practically non-corrosive and which, though hard and tough, may be rolled to sheet form or readily machined without being annealed. It is an alloy of iron, boron, carbon, and copper. The boron is first incorporated in the copper so as to be in excess of the amount that will combine with copper. As the boron associates with iron as readily as silicon, regardless of the carbon content of the iron, the copper is thus caused to alloy with the iron and carbon, forming a homogeneous mixture. By taking 80 parts of Bessemer scrap and fusing it in a furnace and adding 20 parts of copper containing boron in excess, an alloy is produced which may be cast in ordinary sand moulds forming castings homogeneous and easily machined.—*Chemical Engineer.*

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 30, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Skull of Ichthyosaurus, Studied in Serial Sections.*" By Prof. W. J. SOLLAS, F.R.S.

"*The Relation of Excised Muscle to Acids, Salts, and Bases.*" By DOROTHY J. LLOYD.

1. Acids and alkalies both cause swelling in excised muscle. The degree of swelling is not directly proportional to the concentration of acid on alkali in the surrounding fluid, but has a maximum at 0.005 normal for hydrochloric acid and for caustic soda. Alkalies first coagulate and then re-dissolve the muscle substance.

2. The chlorides of the alkali and alkaline earth metals all ultimately coagulate the protoplasm of an excised muscle in isotonic solutions. The bivalent kations show this effect much more rapidly than the monovalent.

3. The iso-electric point for muscle is between $P_{11} = 5$ and $P_H = 7$.

4. It is suggested that the swelling and shrinking of muscles, both in the body and out, is an osmotic phenomenon, and that the state of aggregation of the colloids of the muscle substance is the chief determining factor which fixes the degree of swelling. Lillie's demonstration that acids and alkalies raise the osmotic pressure of gelatin while the neutral salts lower it is in harmony with this view.

5. The osmotic phenomena of muscle can be fully explained without assuming the presence of a semi-permeable membrane round the muscle fibres.

"*The Endemic Flora of Ceylon, with reference to Geographical Distribution and Evolution in General.*" By J. C. WILLIS. (A Correction).

PHYSICAL SOCIETY.

Ordinary Meeting, March 24, 1916.

Mr. F. E. SMITH, A.R.C.S., Vice-President, in the Chair.

A PAPER entitled "*A New Method of Determining Ionic Velocities*" was read by Mrs. C. H. GRIFFITHS, B.Sc.

In the experiments described the cathode, which consists of a horizontal copper disc perforated with two holes, is mounted in a cylindrical glass tube open at the lower end. The whole is suspended from the beam of a balance, and is immersed in a vessel of copper sulphate. The anode is a copper spiral fixed in the electrolyte some distance below the mouth of the cathode vessel. From the rate of change of weight of the suspended system during the passage of a current the ionic velocities can be determined.

DISCUSSION.

Dr. S. W. J. SMITH discussed the paper at some length. At his suggestion his remarks are omitted in order to save space. They will appear in the *Proceedings*.

Mr. F. E. SMITH admired the manner in which small difficulties had been overcome. Some years ago he had determined the electro-chemical equivalent of silver with the anode suspended from a beam of a balance. If Mrs. Griffiths intended continuing these experiments, he would suggest the use of such salts as silver nitrate rather than copper sulphate.

Mr. J. H. SHANBY communicated the following remarks:—It may be noted that the use of a relation, implicit in the reasoning but not actually employed, leads to a simple formula for calculating V without the necessity of separate

determinations of m_1 and m_2 . This saves a rather lengthy calculation, and incidentally avoids the necessity for relying on data in Landolt obtained by other workers. The relation is that the current $Ne(U+V)$ is also equal to $m_1q(U+V)$. (In fact, from the values given, $Ne = 34.36$ and $m_1q = 34.12$). If, then, we substitute

$$\frac{c}{m_1q} - V \text{ for } U \text{ in the equation—}$$

$$m_2V - m_1U - n\epsilon\rho V + \frac{c\rho}{qd} = W \text{ (loss in weight observed),}$$

we have—

$$m_2V - m_1\left(\frac{c}{m_1q} - V\right) - n\epsilon\rho V + \frac{c\rho}{qd} = W,$$

or—

$$V(m_1 + m_2 - n\epsilon\rho) = W + \frac{c}{q} - \frac{c\rho}{qd};$$

i.e.,—

$$Vu(1 - \epsilon\rho) = W + \frac{c}{q} \left(1 - \frac{\rho}{d}\right).$$

The quantity δ is derived from the statement that "total mass of salt in cathode vessel diminishes at the rate of $(m_1 + m_2)Av$ grms./sec." Now this diminution is not by the elimination of salt *qua* salt, but in the form of already dissociated ions. The calculation of δ , from the variation of density of a solution with concentration, lumps together undissociated and dissociated salt. If we may suppose the ions to be of great density, the value of δ would be very small. If we neglect δ and re-calculate V , we find for experiments 12, 9, 3, and 6 respectively the values 6.339, 3.138, 4.011, and 1.561 ($\times 10^{-4}$), leading to the values for $\frac{v}{u+v}$ 0.6584, 0.6561, 0.6627, and 0.6634. For the lowest concentrations these agree with other workers' figures. Metelka's results for densities 1.019 and 1.038 suggest similarly constant values of $\frac{v}{u+v}$ for various concentrations, and are also in good agreement with Mrs. Griffith's figures (as thus re-calculated).

Dr. GRIFFITHS, replying on behalf of Mrs. Griffiths, expressed thanks for the interest taken in the paper by Dr. Smith and for his rational criticism. He agreed that further research was advisable on the density of electrolytically deposited copper, and thought that Mrs. Griffiths might be able to measure experimentally the integral volume changes calculated in the paper. She had already given some thought to these subjects. He was of the opinion that the space above the cathode was ample, and that the value of δ , in so far as its value depended on changes in the concentration of the solution of copper sulphate was correct. If the variations in concentration had been so great as to vitiate the value of δ , then, owing to the equalising effect of diffusion, an appreciable change would have taken place in the weight of the cathode vessel and contents after the conclusion of an experiment.

Mrs. GRIFFITHS has communicated the following comments on Mr. Shaxby's remarks:—The mathematics in the second and third paragraphs appears to be correct and is interesting, but the first paragraph would seem to be somewhat misleading in that the necessity is not avoided for relying on data (dealing with concentrations) obtained by other workers. Mr. Shaxby avoids the necessity by making an hypothesis in the last paragraph which is not justifiable, for when the current has ceased the value of δ cannot depend on the process whereby the salt has been eliminated. Even during the passage of the current the process can have only an inappreciable effect on the value of δ .

A paper entitled "Note on an Explanation of the Migration of the Ions" was read by Dr. S. W. J. SMITH, M.A., F.R.S.

The object of this note is to show how a familiar diagram, appearing in many text-books, can be improved in a way which makes it easier to appreciate what

happens at the electrodes in the simpler examples of Hittorf's method of determining the migration constant. An attempt is made to give precision to an idea which is sometimes vaguely expressed and frequently ignored.

DISCUSSION.

Mr. D. OWEN considered that the usual graphical method expressed the integral effect simply and satisfactorily unless pressed in detail. The analysis of paragraph 3 of the paper, whilst adding precision to the conclusions, did not modify them or "explain" them. The fact of the existence of a volume distribution of electricity near to the electrodes implied an increased potential gradient which played a part in the actions occurring in those regions.

Dr. WILLOWS suggested that, if Mr. Owen's view were correct, it should be possible to detect the potential gradients to which he referred.

Mr. F. E. SMITH remarked that Dr. Smith's paper dealt with a real difficulty, and one which teachers of electricity had to face. He remembered giving lectures on the subject to very elementary students, and feeling dissatisfied with the explanatory diagrams in text-books, had adopted another form of explanation. In dealing with the phenomenon the negative ions were never said to be discharged. The general argument followed was to regard matter as being in four states—solid, liquid, gaseous, and ionic. It was already conceded from analogies that copper ions and metallic copper differed because of a difference of electrical energies. Conversion from one into another could be brought about by adding or subtracting electrical energy. Thus, in the electrolysis of copper sulphate solution with copper electrodes, the electrode at high potential lost energy by conversion of a part of itself into positive ions, and the negative electrode gained energy from the solution due to positive ions giving up their charge and being converted into the metallic form.

Dr. SMITH, in reply, said:—In the original draft of the note, as submitted to the Society, he had hazarded the opinion that perhaps the authors, who used the diagram, wished it to be understood that the excess ions shown at the ends of the chains were removed by excess potential gradients. He had deleted this conjecture, and had substituted a footnote (which was, in fact, a quotation), because he had been unable to find any proof that this was the view taken. In any case it was unsatisfactory. Mr. Owen seemed to imagine that there was some virtue of simplicity about this view which made the analysis of §3 unnecessary. This was not the case. The problem was not merely to state how a Hittorf migration experiment might be supposed to begin. It was as necessary to show clearly what occurred while it continued. This was the object of the note. The analysis of §3 was the simplest general method of expressing the fact that some of the ions which take part in the electrolytic process are fed into the circuit near the electrodes, and are not brought there by the potential gradients. Views which "explain" the facts, while ignoring this, have been the cause of needless confusion in the minds of students. The analysis of §3 showed, for example, that conduction could not proceed as it began unless for every $(u+v)$ cations deposited v cations and v anions were fed into the circuit at the cathode. If the cathode region had to draw upon itself for this supply of ions, the concentration near it would rapidly fall and the "polarisation" at the cathode would rise in accordance with the well-known relation connecting the contact potential difference with the concentration. Diffusion, however, always played an essential part. When it was promoted by convection, a slight reduction in the concentration of the solution round the cathode would be enough to set up an appreciable diffusion current which would be maintained in the way described in §4 of the note. This was the current which supplied the necessary molecules to the cathode space. The relation between this diffusion current and the electric current could be represented by the equation $kn = vi/(u+v)e$,

where k is a diffusion constant, u is the concentration gradient at the cathode, i is the electric current density, and e is the ionic charge.

If notwithstanding this re-expression of his views, which he had thought were adequately conveyed in the note, Mr. Owen still insisted that the usual graphical method was satisfactory, he could think of no better method of convincing him that it was not than to ask him to examine more closely the consequences of his own view as expressed at the meeting. He would then be led to the conclusions stated in the note.

Since the point had been raised, it should, perhaps, be noted that there was an obvious clerical error in the proofs of the paper whereby N , N' , and N'' had been printed throughout instead of SN , $S'N'$, and $S''N''$ respectively. With regard to the question raised by Dr. Willows, he was of the opinion that measurable potential differences of the kind described did not exist. He was glad that the Chairman was of the same opinion as himself with respect to the diagrams and descriptions usually given.

A paper, by Dr. S. W. J. SMITH, entitled "*A Method of Exhibiting the Velocity of Iodine Ions in Solution*" was taken as read. The method was shown.

Dilute solutions of potassium iodide and potassium chloride of equi-molecular concentration have almost the same electric conductivity. They are therefore of interest in connection with the direct measurement of ionic velocities. The paper describes a simple method of observing their common boundary. It is only necessary to add a little mercuric chloride to the potassium chloride solution. An extremely thin layer of mercuric iodide then forms where the two solutions meet. The method is particularly convenient for lecture purposes, and an approximate value of the ionic velocity can be obtained in a few minutes.

The paper gives examples of the use of the method. The current is first passed in the direction which causes the iodine ions to travel towards the chloride. The chlorine liberated at the anode in this case supplies a means of re-determining the velocity of the ions when, the current being reversed, they move in the opposite direction.

THE INSTITUTION OF MINING AND METALLURGY.

PRESIDENTIAL ADDRESS BY SIR R. A. S. REDMAYNE, K.C.B.

(Concluded from p. 167).

3. *Improvement in the Methods in the Dressing and Metallurgical Treatment of Ores.*

In respect of some of our ores there is room for improvement in the methods of extraction of the ore from the gangue or stone and the economic reduction of the ore to the metal. The decision of the Advisory Council to the Committee of Scientific and Industrial Research of the Privy Council to make a grant in aid of the research which the Institution of Mining and Metallurgy and the Royal Cornwall Polytechnic Society are conjointly about to carry out in respect of the economic production of tin and tungsten, with special reference to Cornwall, is a welcome sign of the national awakening which is taking place as to the overwhelming importance of scientific and industrial research.

We are glad and proud to be associated in this good work with a body so old and dignified as the Royal Cornwall Polytechnic Society. Not only does this Society embrace in its membership the most prominent and representative persons in the Duchy, but it holds a high place in the estimation of mining men on account of the excellent and valuable work which it has done in the past in improving the conditions of mining in Cornwall. The idea of carrying out the research of the kind indicated originated largely I believe with the Royal Cornwall Polytechnic

Society, who asked our Institution to undertake the direction of the work.

Nature, duration, and cost of the proposed research.—The research will I presume advance by stages, each stage being dependent on the results obtained in that preceding it. They will probably comprise the following:—

(A) *An investigation of the physical condition of the tin (and wolfram) in the stone*—e.g., degree of fineness, &c.; probably this varies with the depth, being finest at greatest depth. Much work of a scattered and indefinite kind has already been done in this direction and would have to be linked up and completed. Much work could be accomplished in a month. I should think that within three months' time this part of the investigation might be completed.

(B) *Determination of the actual "Percentage of Recovery" at present obtained at the mines, and improvement in the methods of "dressing."*—Curiously enough the precise percentage of recovery now being obtained of cassiterite from the tinstone is at present an unknown quantity, but should, and in my opinion could, easily be established within say two or three months. It is I believe a very low percentage and capable of considerable improvement. I am convinced that it does not exceed 60 per cent, and should and could be increased by improved methods of dressing the ore, which is a purely mechanical process, arrived at by scientific research. Were a resulting improvement of only say 5 per cent secured it would more than warrant the proposed expenditure (£3000), but a much better improvement should be secured. The ore, it may be, is being crushed—

- (a) not sufficiently fine, or
- (b) too fine

for economic classification? Classification methods may be improved? The limits of mechanical methods of extraction will have to be determined, and when this is reached it will be necessary to investigate the value and application of (a) volatilisation and (b) of chemical methods of extraction. It is not possible to estimate with accuracy the length of time which would be absorbed in experimenting with a view of laying down principles on which improved methods of extraction would be based, but a great deal of valuable work could probably be accomplished in six months.

At the outside I do not think the whole investigation will cost more than £5000; certainly not more than £3000 will be expended on the first complete year's work, and this should suffice to establish the vital points. These estimates are based on prolonged and careful consideration, and I think can be accepted as reliable. The whole problem is ripe for solution. Much valuable work was carried out by Prof. Beringer, who died last year when his work was nearing completion.

The Control of the Work of Research.—We are happy in the personnel of our Committee of Control of the research. All the members are well known to you. The Committee of Control will direct the whole of the research work, appointing men to carry out their directions. Such men are available to carry out the work and can start thereon forthwith. Two investigators will be employed at the laboratories, and at the mines there are plenty of persons able and willing to co-operate.

The Committee of Control will make themselves responsible for the work, and will also be responsible to the Council of the Institution of Mining and Metallurgy.

The investigation will be a work of very great utility and should have far-reaching results, and will probably lead to a still wider investigation, viz., into the economic recovery of various "associated" minerals.

4. *The Organisation and Development of Scientific and Industrial Research.*

I have alluded to our connection with the Council of Scientific and Industrial Research, and will quote several expressions of faith from the Memorandum, setting forth

the question of research, which was issued by the Board of Education on July 23 last:—

"There is a strong consensus of opinion among persons engaged both in science and industry that a special need exists at the present time for new machinery and for additional State assistance in order to promote and organise scientific research, with a view especially to its application to trade and industry."

Again:—

"It appears incontrovertible that if we are to advance or even maintain our industrial position we must as a nation aim at such a development of scientific and industrial research as will place us in a position to expand and strengthen our industries and to compete successfully with the most highly organised of our rivals."

And again:—

"It is essential that the Advisory Council should act in intimate co-operation with the Royal Society and the existing scientific or professional associations, societies, and institutes, as well as with the universities, technical institutions, and other institutions in which research is or can be efficiently conducted."

That these are no mere empty expressions of opinion is shown by the action taken by the Council of Scientific and Industrial Research in assisting our proposed scheme of investigation on tin and tungsten. And sentiment has been still further translated into action by a proposal to set up committees of experts in certain branches of industry to advise the Council for Research on matters relating to these industries. In connection with the industries of mining and metallurgy it has decided to set up a committee to deal with (a) the mining of non-metals, (b) metalliferous mining, and a committee for metallurgy dealing with (a) the metallurgy of non-ferrous metals and (b) the metallurgy of iron and steel, and has requested our Council to nominate two members to serve on the Metalliferous Mining Committee and two to serve on the committee relating to the metallurgy of non-ferrous metals, a request to which we have very willingly acceded.

The action of the late President of the Board of Education in securing the appointment of the Advisory Council to the Committee of the Privy Council to ascertain the best methods of securing the organisation and development of industrial and scientific research marks a welcome development, and may lead to great strides being taken in our industrial methods. But it is not sufficient to organise industry and inaugurate research if we have not the material in the shape of highly trained persons to undertake research work, organise and captain industry. Great improvements in our educational system have been carried out during the last twenty years. One has only to point to the rise of the provincial universities, with their great Applied Science departments, to instance this; but we are still behind some of our Continental neighbours. The modern side of our public schools is not what it should be, and the cost of our higher education generally is excessive.

Sir James Dewar, in his Presidential Address to the British Association in 1902, said that—

"the really appalling thing is that the German population has reached a point of general training and specialised equipment which it will take us two generations of hard and intelligently directed educational work to attain. It is that Germany possesses a national weapon of precision which must give her an enormous initial advantage in any and every contest depending upon disciplined and methodical intellect."

But, as the editor of a well known technical periodical in a recent article ("The Organisation of Industry," *Colliery Guardian*, January 21, 1916), in alluding to these words pertinently asks, "Does the nation realise this? For not until it does shall we be able to ensure that State recognition of science without which all the committees under the sun will be but ploughing the sands."

I think the nation does now realise the effectiveness of

the weapon possessed by Germany. If this great war has not brought this home to us nothing else will.

I will conclude by quoting and adapting to my theme the words of one who, if we accept the estimate of Lord Macaulay, was the wisest of mankind, Francis Bacon, who closed his essay on "The True Greatness of Kingdoms and Estates" with these words:—

"No man can by care-taking, as the Scripture saith, add a cubit to his stature in this little model of a man's body, but in the great frame of kingdoms and commonwealths it is in the power of princes or estates to add amplitude and greatness to their kingdoms, for by introducing such ordinances, constitutions, and customs as we have now touched they sow greatness to their posterity and succession. But these things are commonly not observed, but left to take their chance."

NOTICES OF BOOKS.

The Salt and Alkali Industry. By GEOFFREY MARTIN, D.Sc. (Lond.), D.Sc. (Bristol), Ph.D., STANLEY SMITH, M.Sc. (Birmingham), and F. MILSON, B.Sc. (Lond.). London: Crosby Lockwood and Son. 1916. Pp. vii. + 100. Price 7s. 6d. net.

THERE is probably no need nowadays to emphasise the enormous importance of the salt and alkali industry and even the lay public is at any rate beginning to realise that the progress of civilisation is dependent upon it and allied and similar chemical industries. It is to be hoped that there will be in the future a growing demand for textbooks on applied chemistry in the English language, both for works of reference for the expert and for students in training, and the plan of issuing separate manuals such as the present under the editorship of one technological chemist has much to recommend it. The book opens with the common salt industry, and then deals with the manufacture of hydrochloric acid, salt cake, and sodium carbonate in succession. The last subject is treated in rather more detail than the preceding, both the Leblanc and ammonia-soda processes being described and illustrated by schemes and diagrams. However, in order that the book might be of real practical value to the specialist much fuller information would be necessary and more recent and abundant data and statistics. The Stassfurt industry and the preparation of potassium salts are also treated, but only rather sketchily, and the reader who hopes to find any notice of suggestions as to means of working fresh sources of potash will be disappointed.

A Junior Chemistry. By W. WILLINGS, B.Sc. London, Glasgow, and Bombay: Blackie and Son, Ltd. 1916. Pp. viii. + 280. Price 2s. 6d.

THE course of elementary chemistry given in this book is mainly observational, the laws of chemistry and the atomic theory being deferred until quite the end. The usual experiments beginning with some on solution, crystallisation, distillation, &c., are well described, and some fairly complicated and difficult ones are included, such as the determination of the composition of water by weight. Some of the metals are included for treatment, short accounts being given of the extraction of them from their ores and of their properties, and those of their principal compounds. Some historical notes are inserted at various places throughout the text, and at the end of each chapter a few questions are given, many of them being taken from the Oxford and Cambridge Local Examinations. While not standing out in any striking manner from the many good text-books of elementary practical and descriptive chemistry for beginners which are to be had, the book contains clear directions for the carrying out of upwards of a hundred experiments by which the pupil should acquire some skill in manipulation, and the results and conclusions to be drawn from them are logically discussed.

The Journal of the Institute of Metals. Vol. XIV. Edited by G. SHAW SCOTT, M.Sc. London: The Institute of Metals. 1915.

THIS number of the *Journal of the Institute of Metals* contains the May Lecture of last year, delivered by Sir J. J. Thomson, the subject of which was the Conduction of Electricity through Metals. Other papers include a long and exceedingly valuable one by Mr. W. B. Parker upon Specifications for Alloys for High-speed Steel Turbine Blading. This paper was followed by a detailed discussion, of which a full report is given, and all who took part in the discussion recognised the great importance of the work described in the paper. Another valuable contribution was that on Metallic Crystal Twinning by Direct Mechanical Strain, by Prof. C. A. Edwards, of Manchester University, which was illustrated by remarkable photographs. The Journal also contains abstracts of papers dealing with the non-ferrous metals and the industries connected with them, published in recent periodicals of many nations.

Analysis of Natural Gas and Illuminating Gas by Fractional Distillation at Low Temperatures and Pressures. By G. A. BURRELL, F. M. SEIBERT, and J. W. ROBERTSON. Washington: Government Printing Office.

THIS bulletin contains a description of the experiments performed by the authors in the investigation of a method of separating and determining the hydrocarbons in gaseous fuels by fractional distillation *in vacuo* at low temperatures. This method has been applied with satisfactory results to the separation of the hydrocarbons in specimens of natural gas from Pittsburgh, Pa., and also to the separation of illuminants in artificial illuminating gas. A detailed account is given of the procedure, which is based upon the liquefaction of the gas under investigation, followed by fractional distillation, and which is the only known method applicable to the separation of some hydrocarbons. Methane can readily be removed at the temperature of liquid air, ethane at -150° to -140° , and benzene can be determined in mixed gases by removing carbon dioxide and water vapour, cooling to -78° , removing the other gases at this temperature, and finally vapourising the benzene and reading the vapour pressure on a mercury manometer.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii. No. 9, February 28, 1916.

Stability of Hypochlorites in very Dilute Solutions. Consequences from the Point of View of their Use in the Sterilisation of Water (Javelisation).—Lucien Valléry.—The author's study of the stability of hypochlorites in very dilute solutions has given results which, although incomplete, are important from the point of view of the use of these substances for the sterilisation of water. Using solutions containing from 1 to 5 parts per million of active chlorine the author has shown that the hypochlorites undergo slow decomposition which may be limited or not, according to the original strength, and the limit of which when it exists is greatly influenced by apparently slight variations in the medium. The velocity of this decomposition when normal seems to be representable analytically by a portion of an equilateral hyperbola, but the author cannot yet affirm this definitely. As regards the effect of variations of the medium upon the

decomposition of hypochlorites it seems that two actions must be distinguished:—(i.) A purely catalytic action, positive or negative; (ii.) a purely chemical action due to the presence in the medium of substances capable of reacting either with the molecule of hypochlorite or with the products of its decomposition.

Detection of Free Chlorine in Town Waters.—G. A. Le Roy.—When active chlorine, in the form of hypochlorites of the alkalis or alkaline earths, is introduced into water for the purpose of purifying it, it is rapidly transformed into inactive and combined chlorine, the process being more or less rapid according to the nature of the water, the amount of organic matter it contains, &c. When more than about 0.05 mgrm. per litre of active chlorine is present the taste and smell of the water become disagreeable to the consumer. The chemical control of waters which have been treated with hypochlorite is thus of obvious importance. Unfortunately the reagents which detect active chlorine when present in very small quantities, even iodide of starch, which is the best of them, are useless when the amount of chlorine per litre is less than about 0.05 mgrm. The author has suggested an analytical method of determining chlorine based upon the fractional freezing of the water, the freezing being performed in such a way as to eliminate the greater part of the water in the form of pure ice, while the active chlorine migrates into the unfrozen water. About 10 litres of water must be used, and it must be frozen in a metal receptacle with enamelled walls. Care must be taken not to agitate the vessel. When about a fiftieth of the volume of the water is left the chlorine in it may be detected by the usual reagents. By this method about 0.0005 mgrm. of active chlorine per litre can be detected.

MISCELLANEOUS.

City and Guilds of London Institute.—The Executive Committee have appointed Prof. Gilbert T. Morgan, D.Sc., F.R.S., of the Royal College of Science, Dublin, to the Chair of Chemistry of the Institute's Technical College, Finsbury, rendered vacant by the death of Prof. Meldola. Prof. Morgan was a former student at the College under Prof. Meldola, and later for some years chemist in the works of Messrs. Read, Holliday, and Sons. He is a recognised authority on synthetic chemistry and dye-stuffs, on which subjects he has published many original papers. He will take up his duties at the College after Easter.

Research Scheme.—In the March number of the *Journal of the Society of Dyers and Colourists* details are given of the research scheme instituted in March, 1914, by the Council of the Society. This scheme, the development of which has been somewhat retarded by the war, is now established upon a working basis, and a list of researches for which suitable investigators have already been found has been compiled. A list is also given in the Journal of proposed additional researches for which no investigators have been nominated and for which the Council are prepared to make grants, varying from £25 to £200, to competent investigators. The suggested subjects include the following:—A satisfactory method of producing a good black on Tussah silk; the dyeing of kemps in woollen yarn or pieces; the dyeing of a black on cotton yarn to stand a chlorine bleach, and to be fast to rubbing, at a cost not exceeding that of an ordinary aniline black; the dyeing of dead cotton present in cotton yarn or piece goods, &c.

MEETINGS FOR THE WEEK.

WEDNESDAY, 19th.—Microscopical, 8. "Early Stages in the Evolution of Life," by B. Moore. "Studies in Marine Biology," by F. Martin Duncan. "Some Suggestions regarding Visual Efficiency in the Use of the Microscope and other Optical Instruments," by J. W. Purkiss.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2943.

TWO METHODS OF SEPARATION OF THE METALS OF THE ALKALINE-EARTH GROUP.

By ALICE G. PATERSON.

BOTH methods are based on the slight differences in solubility of the relatively insoluble salts of the group, both being applications of the principle involved in fractional precipitation.

According to this principle, as is well known, if a precipitating agent, such as ammonium carbonate, is added to a solution containing a mixture of salts of metals whose carbonates are relatively insoluble, such as those of the alkaline earths, the least soluble carbonate is the one to be first precipitated. The carbonates continue to be precipitated in order of their solubility, with exceptional action only in the case of very high concentration. However, if barium, for instance, is precipitated as a carbonate and then a solution of a sulphate is added it is converted into the less soluble sulphate; also if barium is precipitated as a carbonate and a solution of a strontium salt is then added barium carbonate dissolves, strontium carbonate being formed.

If, then, two or more precipitating agents are added to a solution containing a mixture of salts, any given metallic ion will unite with that acid ion which forms the least soluble salt.

This principle is employed by Stieglitz ("Qualitative Chemical Analysis," xi., p. 21, "Separation and Determination of Strontium"), also by A. A. Noyes ("Qualitative Chemical Analysis," p. 85). In the present instance the writer proposes its application to the group analysis.

The first method is as follows:—The solution, containing salts of the alkaline-earth metals, is treated with excess of solutions of ammonium carbonate and ammonium sulphate together. Barium precipitates as sulphate and calcium and strontium as carbonates. This mixture is brought to boiling and allowed to stand twenty to thirty minutes, with occasional stirring, as it has been found that the action is not immediately complete. Especially is this true in the presence of magnesium salts. Some magnesium may also be precipitated as magnesium ammonium carbonate. The mixture is then filtered and the precipitate washed until free from precipitating agents. The precipitate is washed into a beaker, using as small an amount of water as possible, and 1.5 volumes of 1 per cent acetic acid added, and the mixture brought to boiling, dissolving the carbonates and driving off carbon dioxide. Enough acid should of course be present to complete this action. The undissolved precipitate is barium sulphate. This is filtered off, using paper pulp; the precipitate is washed and barium confirmed by the flame. The filtrate contains the acetates of calcium and strontium, possibly also some magnesium acetate. This filtrate is made slightly alkaline with ammonium hydroxide, is then treated with excess of ammonium carbonate and ammonium oxalate together, and the mixture is brought to the boiling-point with stirring. It is then allowed to stand twenty to thirty minutes with stirring, is filtered, and the precipitate washed until free from precipitating agents. This precipitate consists of calcium oxalate and strontium carbonate. It is washed from the paper with a small amount of water, and 1.5 volumes of 1 per cent acetic acid added, and the mixture stirred or shaken vigorously for a few minutes to dissolve the strontium carbonate and expel the carbon dioxide. As before, enough acid should be present to complete this action. It is then filtered, and the residue,

consisting of calcium oxalate, washed. The filtrate is made slightly alkaline with ammonium hydroxide and the strontium then precipitated with ammonium sulphate or ammonium carbonate, evaporating the solution if the volume is large, and confirmed with the flame, as is also the calcium in the calcium oxalate.

In the presence of both the carbonate and oxalate ion the strontium is apparently nearly completely precipitated as carbonate and the calcium as oxalate, provided a little time is allowed for the action to complete itself. In the absence of calcium the entire precipitate formed upon the addition of ammonium carbonate and ammonium oxalate consists of the carbonate of strontium, and dissolves easily in acetic acid. In the absence of strontium the entire precipitate consists of the oxalate of calcium. This is only very slightly soluble in cold 1 per cent acetic acid, so that in the absence of strontium a very faint cloudiness results when the acetic acid solution is treated with ammonium carbonate. This solubility seems to decrease if the precipitate is allowed to stand the twenty to thirty minutes before filtering. A small amount of magnesium may appear here as magnesium oxalate, distinguishable from calcium by the flame.

The two most important points for a clear-cut separation are, first, the sufficient washing of the precipitates, and second, allowing the precipitates to stand before filtering. In this respect the method does not differ from others. If the washing is not thorough and the sulphate ion remains in soluble form with the residue of insoluble sulphate and carbonate it will of course combine with the strontium ion when the strontium carbonate is dissolved by acetic acid, thus causing strontium sulphate to remain in the residue with barium sulphate. In regard to the second point, the time is probably necessary because the solubilities of certain of the salts are so nearly the same, as, for instance, that of barium sulphate and barium carbonate and that of strontium sulphate and strontium carbonate, that time must be allowed for complete reversion to the less soluble of the two, although the action is nearly complete after simply heating the mixture. This seems to be indicated by the fact that when the precipitate of carbonates and sulphates was *not* so allowed to stand before filtering some barium appeared in the solution of acetates of strontium and calcium, even when the mixture was subsequently only warmed and not boiled with 1 per cent acetic acid; also, that when the mixture *had* been allowed to stand, even bringing to a boil with 1 per cent acetic acid showed no barium in the filtrate. This seems to be also true in the case of the strontium carbonate and calcium oxalate. If filtered at once, after the addition of the precipitating agents or after a few minutes of warming, neither the calcium flame, when a small amount of calcium is used, nor the strontium, when a small amount of strontium is used, is pure. As the following experiments will show, this is not the case when the mixture of precipitates stands after being heated.

In the following experiments the mixture analysed contained in every case 5 cc. of a normal solution of barium chloride, 5 cc. of a normal solution of calcium chloride, and 5 cc. of a normal solution of magnesium chloride, together with the amount of strontium salt specified. This was precipitated with 15 cc. ammonium sulphate solution (M) and 15 cc. ammonium carbonate solution (250 grms. to the litre), and analysed according to the foregoing outline. In every case enough water was first added to the solution to make the total volume 100 cc. No ammonium chloride was used. In the first five experiments following the mixture was filtered immediately after being heated with the precipitating agents. In the last two (6 and 7) the mixture stood thirty minutes before being filtered and no barium appeared in the filtrate. Boiling with 1 per cent acetic acid, after being thus allowed to stand, did not affect barium. Apparently a small amount of barium is present as barium carbonate when precipitation is first effected. This is probably completely changed to barium sulphate on standing a short time.

- (1) 0.5 cc. 0.1/N SrCl₂ Mixed ppt. of carbonate and sulphate boiled with 5 p.c. HAC. Distinct ppt. when tested for Sr with ammonium carbonate. Indeterminate flame.
- (2) 0.7 cc. 0.1/N SrCl₂ Mixed ppt. of carbonate and sulphate boiled with 5 p.c. HAC. Distinct ppt. when tested for Sr with ammonium carbonate. Mixed flame.
- (3) 1 cc. 0.1/N SrCl₂ Mixed ppt. of carbonate and sulphate boiled with 1 p.c. HAC. Distinct ppt. when tested for Sr with ammonium carbonate. Ca and some Ba in flame.

The main barium sulphate residue after being thoroughly washed showed no calcium or strontium flame.

- (4) 1 cc. 0.1/N SrCl₂ Mixed ppt. of carbonate and sulphate boiled with 1 p.c. HAC. Ammonium sulphate used to precipitate Sr. Slight ppt. Barium flame with trace of strontium.
- (5) 1.5 cc. 0.1/N SrCl₂ Mixed ppt. of carbonate and sulphate warmed, not boiled with HAC. Ammonium sulphate used to test for Sr. Slight ppt. Sr and Ba flame.
- (6) 1.5 cc. 0.1/N SrCl₂ Stood 30 minutes after the addition of precipitating agents. Mixed ppt. warmed, not boiled with 1 p.c. HAC. Ammonium sulphate used to test for Sr. No ppt. even on heating.

From Experiments 5 and 6 it would appear that if the mixed precipitate is allowed to stand before filtering, barium does not go into solution.

- (7) 2 cc. 0.1/N SrCl₂ Stood 30 minutes after the addition of precipitating agents. Mixed ppt. boiled with 1 p.c. HAC. Stood 20 minutes with ammonium carbonate and ammonium oxalate. Ammonium sulphate used to test for Sr. Slight ppt. Solution evaporated and precipitated with ammonium carbonate. Considerable precipitate; fine, pure strontium flame. No barium.

2 cc. 0.1/N SrCl₂ = 8.7 mgrms. of strontium.

In the following experiments the mixture analysed contained in every case 5 cc. N barium chloride solution, 3 cc. N strontium chloride solution, 5 cc. N magnesium chloride solution, together with the amount of calcium salt specified. Total volume of solution made up to 100 cc. No ammonium chloride used. Procedure the same as in preceding experiments. In Experiments 1 and 2 the mixture of precipitated oxalate and carbonate was filtered immediately after being brought to boiling with the precipitating agents. In Experiment 3 this mixture was allowed to stand twenty minutes before filtering.

- 1) 1.5 cc. 0.1/N CaCl₂ 5 p.c. HAC used for both separations. Cloudy residue for calcium. Red flame, not free from strontium.

- (2) 2 cc. 0.1/N CaCl₂ 1 p.c. HAC used for both separations. Distinct residue for calcium. Mixed flame.
- (3) 2 cc. 0.1/N CaCl₂ 1 p.c. HAC used for both separations. Stood 20 minutes with ammonium carbonate and ammonium oxalate before filtering. Slight residue; fine calcium flame.

2 cc. 0.1/N CaCl₂ = 4 mgrms. of calcium.

In the following experiments the mixture analysed contained in every case 5 cc. N calcium chloride solution, 5 cc. N strontium chloride solution, 5 cc. N magnesium chloride solution, together with the specified amount of barium chloride. Total volume, 100 cc. Procedure the same as in the preceding experiments. In Experiments 1 and 2 the precipitate of sulphate and carbonate was filtered immediately after being heated with the precipitating agents. In Experiment 3 this precipitate was allowed to stand thirty minutes after heating before it was filtered.

- (1) 0.5 cc. 0.1/N BaCl₂ Mixed ppt. of sulphate and carbonate boiled with 1 p.c. HAC. Very slight residue. No flame test obtainable.
- (2) 1 cc. 0.1/N BaCl₂ Mixed ppt. of sulphate and carbonate boiled with 1 p.c. HAC. Very slight residue. Barium flame.
- (3) 1 cc. 0.1/N BaCl₂ Mixed ppt. of sulphate and carbonate stood 30 minutes. Boiled with 1 p.c. HAC. Considerable residue; strong barium flame.

1 cc. 0.1/N BaCl₂ = 6.8 mgrms. of barium.

Experiments 2 and 3 are the same except for the difference of time. In 2 probably some of the barium remains as barium carbonate, dissolving in the acetic acid.

These amounts could be easily detected, giving decided residue and good flame tests.

The second method makes use of the same principle, with somewhat different application. In this method strontium sulphate is dissolved by the use of lead acetate, the less soluble lead sulphate being formed.

The solubilities (Stieglitz) of the sulphates of the alkaline-earth metals and of lead sulphate are as follows, given in mols. per litre:—BaSO₄, 0.041; SrSO₄, 0.0502; CaSO₄, 0.015; PbSO₄, 0.0313.

It will be seen that lead sulphate lies between barium sulphate and strontium sulphate. If lead acetate is added to a suspension of calcium sulphate, strontium sulphate, and barium sulphate in water, calcium and strontium go into solution as acetates, lead sulphate being precipitated. Barium sulphate is not affected.

The method is as follows:—A part of the solution is first tested for barium with potassium chromate and the flame. The remainder of the solution, without removing barium, is then treated with ammonium chloride, and precipitation effected with ammonium sulphate, the mixture being brought to boiling. Most of the calcium remains in solution. Barium and strontium, with perhaps a small amount of calcium, are precipitated as sulphates. These are filtered off through paper pulp, washed twice, and then transferred by washing to a beaker and treated with an excess of lead acetate solution (N). This mixture is warmed, not boiled, for a few minutes and filtered. The filtrate contains strontium acetate, the excess of lead acetate, and probably a small amount of calcium acetate. The residue contains lead sulphate and barium sulphate. The filtrate is freed from excess of lead by hydrogen su

phide, and is then tested for strontium with ammonium sulphate or with carbonate and oxalate according to Method 1.

It appears from the following experiments that if the mixture is boiled with lead acetate some barium goes into solution. (Experiments 1 and 2). If, however, the mixture of sulphates is warmed but not boiled with lead acetate barium does not dissolve, while strontium does. (Experiments 3 and 4).

In every case the solution analysed contained 5 cc. N barium chloride solution, 5 cc./N Ca solution, and 5 cc. N magnesium chloride solution, together with the specified amount of strontium. Total volume, 100 cc.

- (1) 0.3 cc. 0.1/N SrCl₂ Precipitated sulphates boiled with lead acetate solution. Distinct cloudiness when testing for strontium with ammonium sulphate. Barium flame.
- (2) No SrCl₂ Same as preceding experiment. Barium flame.
- (3) No SrCl₂ Precipitated sulphates warmed but not boiled with lead acetate solution. No precipitate when tested with ammonium sulphate. Barium not dissolved.
- (4) 1 cc. 0.1/N SrCl₂ Precipitated sulphates warmed but not boiled with lead acetate. Distinct cloudiness when tested for strontium with ammonium sulphate. Strontium separated by carbonate oxalate method. Gave fine, pure strontium flame.

1 cc. 0.1/N SrCl₂ = 4.3 mgrms. of strontium.

The principle may have a wider application in general analytical work, and perhaps even possesses some value for quantitative separations. It may be seen that there are possibilities for very clear-cut and complete separations. The two methods as given work out rapidly and very satisfactorily. The writer has made use of the first method in the laboratory with students in the first semester of qualitative analysis with very good results.

There arises the possibility of precipitating several metals by the use of two or more precipitating agents and then by the addition of a soluble salt of a metal not under examination, dissolving one or more of those precipitated, or, several salts having been precipitated by one reagent, a similar displacement being carried out. For instance, possibly the carbonate, oxalate, and sulphate could all be used together to precipitate barium, calcium, and strontium, these then being separated, first by the use of acetic acid, then dilute hydrochloric acid. Also, in precipitating calcium oxalate and strontium carbonate together, lead acetate might be used to dissolve calcium oxalate, leaving strontium carbonate, since the solubility of lead oxalate is less than that of calcium oxalate, but the solubility of lead carbonate is somewhat greater than that of strontium carbonate. The writer has not, however, carried out these separations. A large difference in solubility does not seem to be necessary—is not in fact desirable for the carrying out of such schemes.

A separation of copper and cadmium may be made by warming a suspension of the sulphides in water with lead nitrate solution. Cadmium sulphide dissolves, copper sulphide is not affected. The excess of lead is removed with ammonium sulphate and cadmium precipitated as a sulphide. The objection to this method is that neither ammonium sulphate nor dilute sulphuric acid completely removes the lead, so that in testing for cadmium the solution is slightly discoloured by lead sulphide. This, however, is the case in the usual scheme of analysis whenever lead is present.

The writer expects to continue work on this subject.—*Journal of the American Chemical Society*, xxxvii., No. 10.

A NEW TEST FOR COPPER.*

By W. G. LYLE, L. J. CURTMAN, and J. T. W. MARSHALL

(Concluded from p. 175).

Zinc.—Table V. gives the results obtained with solutions of zinc of strength 100 mgrms. in 1 cc.

TABLE V.

Volume before the addition of reagent, 1.1 cc.; 1 cc. 0.40 per cent NaC₂H₃O₂; 1 cc. of reagent.

No.	Mgrm. Zn.	Mgrm. Cu.	Result.
1, 2.	100 as Zn(NO ₃) ₂	0.01	Precipitate.
3.	100 as Zn(NO ₃) ₂	0.00	"
4.	100 as ZnSO ₄	0.00	"
5, 6.	200 as ZnSO ₄	0.10	Immediate precipitate.
7, 8.	200 as ZnSO ₄	0.00	Negative in one hour.

These results find their explanation in the acidity contributed by the zinc salt. 200 mgrms. of Zn gave a higher hydrogen ion concentration to the solution than that given by 100 mgrms., and as a consequence no precipitate was obtained in Experiments 7 and 8. If this explanation be correct 1 mgrm. of Zn should give a better test than 100 mgrms. Experiments showed not only that this was the case, but also that *n*-aminocaproic acid is a fairly sensitive reagent for the detection of small amounts of zinc, as shown in Table VI.

TABLE VI.

Solution ZnSO₄, 1 cc.; 1 cc. of 40 per cent NaC₂H₃O₂; 1 cc. of reagent.

No.	Mgrm. Zn.	Result.		
		1 min.	2 min.	5 min.
1.	0.05	Good.	Strong.	Strong.
2.	0.03	Negative.	Good.	Very good.
3.	0.02	"	Negative.	Very faint (limit).
4, 5.	0.01	"	"	Negative.

The results in Table VI. show that under the conditions employed in testing for copper the reagent is capable of detecting 0.02 mgrm. of zinc. Since the reagent is sensitive to small quantities of zinc there was need for a means of differentiating between zinc and copper if the test were to be applied to unknown solutions. After some experimentation it was found that zinc does not precipitate when the hydrogen ion concentration (*p*-nitrophenol as indicator exceeds 10^{-5.5}). If to an acid solution of zinc containing aminocaproic acid and a drop of *p*-nitrophenol solution (0.04 per cent) sodium acetate be added a yellow colour will develop, which deepens on further addition of acetate. When the colour is only a faint yellow (*C_H* + = 10^{-5.2}) no zinc will come down. Not until sufficient sodium acetate has been added to give a strong yellow colour (*C_H* + = 10^{-5.8}) will the zinc precipitate in five minutes. The results in Table VII. show the reliability of the method.

TABLE VII.

Volume, 2 cc.; one drop *p*-nitrophenol; adjusted to light yellow colour with sodium acetate and 0.1 N HCl; 1 cc. reagent.

No.	Mg. Zn.	Mg. Cu.	Result.
1 to 5.	1.0	0.000	Negative in five minutes.
6 to 10.	1.0	0.004	Positive in five minutes.

Mercury.—The following solutions were used in the experiments with mercury, viz.:—Solution A, Hg 10 per cent (as nitrate) in 2 per cent concentrated HNO₃; Solution B, Hg 10 per cent (as chloride) in 5 per cent NaCl solution (the NaCl was added to increase the solubility of HgCl₂); Solution C, Hg 1 per cent. (as chloride) in H₂O.

1 cc. each of Solutions A, B, and C was treated with 1 cc. of 40 per cent $\text{NaC}_2\text{H}_3\text{O}_2$ and 1 cc. of the reagent. A fair test was obtained with Solution A, B was negative, while Solution C gave a strong test.

These results indicated that the presence of NaCl prevented the precipitation of the mercury. To further test this conclusion the following experiments were made:—

TABLE VIII.

Volume after the addition of 1 cc. of 40 per cent $\text{NaC}_2\text{H}_3\text{O}_2$, 3 cc.; 1 cc. of the reagent.

No.	Mg. Hg. (Sol. A).	Mg. Cu.	20 p.c. NaCl cc. (a)	Result.	
				5 min.	10 min.
1.	100	0.00	0.0	+	+
2—5.	100	0.00	1.0—0.5	—	—
6—8.	100	0.01	1.0—0.5	+	+
9.	1	0.00	0.0	Immediate heavy ppt. Negative.	
10—11.	1	0.00	0.5—0.1		

- (a) The addition of NaCl to the Hg solution causes the formation of an exceedingly faint cloud, due probably to HgCl_2 in suspension. The solution clears up somewhat on the addition of the aminocaproic acid. However, in no case was this cloud found to interfere with the test. In the many experiments made the controls never showed the characteristic "crawl," while in the presence of copper decided tests were obtained.

TABLE IX.

Experiments with HgCl_2 solutions. 1 cc. 40 per cent $\text{NaC}_2\text{H}_3\text{O}_2$; 1 cc. reagent (a).

No	Mg. Hg. (Sol. B).	Mg. Cu.	20 p.c. NaCl cc.	Result.	
				5 min.	10 min.
1—2.	100	0.00	0.0	—	—
3—4.	100	0.01	0.0	+	+
5. (b)	1	0.00	0.0	Immediate heavy ppt. Negative in 10 min. Negative in 10 min.	
6. (c)	1	0.00	0.5		
7. (c)	1	0.00	0.1		

- (a) In tests 1—4 the volume of the solution before the addition of the reagent was 2 cc.
(b) In tests 5—7 the volume of the solution before the addition of the salt was 1 cc.
(c) At the end of ten minutes 9 mgrms. of Hg were added slowly from a pipette to these tubes. No precipitate formed in ten minutes.

The results of the table show that the addition of NaCl will prevent the formation of basic salt or aminocaproate in solutions of mercury. Before concluding our work with this metal we determined that small amounts may also be prevented from precipitating by regulating the acidity as in the case of zinc.

Iron and Aluminium.—In the presence of 100 mgrms. of either of these metals in the form of chlorides we were unable to get positive tests with 0.05 mgrm. of copper or less. This is due to the fact that before the acidity can be depressed sufficiently to permit the precipitation of small amounts of copper (C_{11} + about 10—4) these metals (also Cr) separate in the form of hydroxides and mask the reaction. After much experimenting the following procedure was found efficient: 100 mgrms. of Fe or Al in the form of their chlorides were mixed with 0.05 mgrm. Cu as nitrate. The mixture, the volume of which was about 2 cc., was slowly poured with constant stirring into 3 cc. NH_4OH (1:1); the solution was filtered through a fluted filter and the precipitate washed with 2 cc. of water. The combined filtrate and washings were evaporated to dryness and the ammonium salts removed by heating with KOH. The solution was then made acid with HCl, evaporated to one drop, taken up with 1 cc. of water, and tested in the usual manner. By this procedure good tests were consistently obtained in three minutes.

Chromium.—A 10 per cent solution of Cr as $\text{Cr}(\text{NO}_3)_3$ was used in this work. 1 cc. of this solution, to which

0.05 mgrm. of copper were added, failed to give the test. Precipitation with NH_4OH , as in the procedure for Fe and Al, did not serve in this case owing to the appreciable solubility of $\text{Cr}(\text{OH})_3$ in ammonia. The filtrate always contained sufficient chromium to confuse the test.

To determine whether the oxidation of the chromium to chromic acid would eliminate the interference of this metal tests were made for copper in the presence of K_2CrO_4 . The results showed that 100 mgrms. of Cr as chromate did not prevent the precipitation of 0.01 mgrm. of Cu. Subsequent experiments, however, starting with the metal as nitrate and oxidising to chromate with sodium peroxide, did not give consistent results.

After oxidation it was necessary to make the mixture acid in order to keep the copper in solution. In this connection a difficulty was encountered in attempts to adjust the acidity, for the test, even when 1 cc. of 40 per cent sodium acetate is used, cannot be applied if the initial acidity is too great. Again, the strong colour of the chromate solution does not permit the use of the indicator, without which it would be impossible in an unknown solution to determine whether the test were due to the presence of copper or zinc. It was therefore necessary to remove the CrO_4 . The chromate was dissolved in about 10 cc. of water, 1 cc. of NH_4OH (1:1) added, the mixture heated to boiling and an excess of BaCl_2 added. This procedure appeared sound, first because the presence of barium would not interfere with the test, and second because BaCrO_4 being crystalline would not adsorb appreciable quantities of copper. The filtrate from the BaCrO_4 was evaporated just to dryness, taken up with 1 cc. of water, and refiltered through a very small filter into a test-tube. One drop of *p*-nitrophenol was then added, the acidity adjusted to a faint yellow, and 1 cc. of the reagent added. The following results were obtained:—

TABLE X.

No.	Mg. Cr as K_2CrO_4 .	Mg. Cu.	Mg. Zn.	Result.	
				1 min.	5 min.
1.	100	0.05	0.0	Good test in 1 min. Negative test in 5 min.	
2.	100	0.00	0.1		

At the expiration of five minutes the contents of Tube 2 were divided into two portions. 0.02 mgrm. of Cu added to one portion gave a good test, showing that the conditions were favourable for the precipitation of copper. To the other portion 0.1N NaOH was added till a strong yellow colour developed. A copious precipitate was then obtained, showing the presence of zinc.

Nickel and Cobalt.—The reagent is capable of detecting 0.01 mgrm. of copper in the presence of 100 mgrms. of either of these metals. (With some preparations of the nitrates of nickel and cobalt only very faint tests were obtained in five minutes; on standing for ten or fifteen minutes, however, the tests improved decidedly). Although the aminocaproates of nickel and cobalt are fairly insoluble (according to Kudielka, *loc. cit.*, the solubility of the nickel salt is about 29 parts in 100,000; that of the cobalt salt is 21 parts in 100,000) these salts are not formed under ordinary conditions when C_{11} + > 10—7. Thus they are much more sensitive to acid than the corresponding zinc salt, and consequently conditions permitting the differentiation between copper and zinc will completely prevent the precipitation of nickel and cobalt. Although the results showed that under our conditions (1 cc. 40 per cent sodium acetate as buffer) (Kahlbaum's "Zur Analyse") nickel and cobalt remained in solution, a small decrease in the hydrogen ion concentration, such as might be caused by a trace of alkali in the sodium acetate or by heating the mixture, would bring about a slight precipitation of these metals. Consequently in an unknown solution, when 1 cc. of 40 per cent sodium acetate is used as a buffer, a positive test cannot be regarded as conclusive for copper because of the possible presence not only of zinc but also of nickel and cobalt. The strong colour of solutions of nickel and cobalt pre-

cludes the use of *p*-nitrophenol as an indicator for adjusting the acidity. We know of no feasible method whereby a separation of 0.01 mgrm. of copper from 100 mgrms. of nickel or cobalt can be effected. We therefore recommend in such cases the following procedure:—To the neutral or faintly acid solution add 1 cc. of 40 per cent sodium acetate and 1 cc. of aminocaproic acid; allow the mixture to stand for about one-half hour (this is to ensure complete precipitation; frequent agitation is advantageous). The precipitate, which may consist of aminocaproates of Cu, Zn, and traces of Ni and Co, is collected on a small filter, thoroughly washed, and then dissolved in hot dilute HCl. The filter is well washed, the combined solution and washings concentrated, *p*-nitrophenol added, the acidity adjusted to a pale yellow, and finally 1 cc. of aminocaproic acid added. A precipitate proves the presence of copper. Following this procedure good tests were obtained from solutions containing 0.02 mgrm. of copper and 50 mgrms. of nickel or cobalt in a volume of 1 cc. In the absence of copper this method gave good controls.

Procedure for Unknowns containing all Metals.—We do not know of a systematic procedure whereby any of the sensitive reagents hitherto employed for the detection of minute amounts of copper can be applied to solutions containing all the common metals. The great difficulty encountered in such cases is to be found in the tendency of precipitates, particularly those of a gelatinous character, to adsorb appreciable quantities of copper. Based on our experience with the test when applied to the metals individually, we would suggest the following procedure, observing the precautions necessary in quantitative work. After the removal of the silver group by means of HCl the filtrate and washings are treated with an excess of KOH, heated and filtered. The precipitate is then dissolved in HCl and evaporated to a few drops. More HCl is added and the solution again evaporated to a few drops. The diluted solution is then poured into an excess of NH_4OH and filtered. The filtrate is evaporated to dryness and boiled with KOH to remove ammonium salts. The solution is then acidified with HCl and heated to dissolve the CuO . (If the solution is coloured and the indicator cannot be satisfactorily employed recourse must be had to the procedure recommended for Ni and Co). One drop of *p*-nitrophenol is added, the acidity adjusted, and test applied.

Remarks concerning the Comparative Merits of the Reagents in Copper.—*N*-Aminocaproic acid possesses an important advantage over all the other reagents used for the detection of small amounts of copper in that, when the simple precautions to avoid the interference of zinc or mercury are taken, the test is highly characteristic and specific for copper.

It appears to be more delicate than the ammonia test according to the figures given by Pritz, Guilanden, and Withrow (*Journ. Am. Chem. Soc.*, 1913, xxxv., 168), and it possesses the further advantage that the interference of nickel may be readily overcome. Experiments with 0.004 mgrm. of copper gave decided tests with *n*-aminocaproic acid, but with ferrocyanide the tests were not evident except when compared with the blank; moreover with ferrocyanide the colour, even with considerable amounts of copper, could not be distinguished from that of the control when examined at night. Again, with the ferrocyanide test there are many more metals which interfere than is the case with aminocaproic acid. Solutions containing amounts of Fe, Ni, Co, Pb, Cd, Mn small enough to permit the use of an indicator may be tested directly with aminocaproic acid. Thus the almost universal presence of traces of iron, which would prevent the direct use of the ferrocyanide test, will not interfere in the least with the aminocaproic acid test. Ammonium sulphide has also been recently shown to be an exceedingly sensitive reagent for copper (*Journ. Am. Chem. Soc.*, 1913, xxxv., 168), but the large number of metals which interfere materially limits its usefulness. At the present time the cost of *n*-aminocaproic acid greatly ex-

ceeds that of the other reagents, but it is believed that its great usefulness will serve to cheapen it considerably. It is, moreover, a simple matter to recover the acid from waste solutions, so that the same supply can be used repeatedly.

Experiments are now in progress in the Harriman Research Laboratory, Roosevelt Hospital, New York City, to determine the behaviour of the rarer elements with *n*-aminocaproic acid, and also the conditions under which the reagent may be applied as a specific test for zinc. The use of this reagent for the purposes of quantitative analysis is also under consideration.

Summary.

1. It has been shown that an aqueous solution of normal aminocaproic acid is an exceedingly sensitive reagent for the detection of copper. With this reagent 0.004 mgrm. of copper may be detected with certainty.

2. Mercury and zinc are the only other common metals which yield, under the conditions specified, a precipitate with the reagent. The interference of the former may be overcome by the addition of sodium chloride; the latter may be prevented from precipitating by adjusting the acidity of the solution.

3. Procedures have been given for the detection of small amounts of copper in the presence of relatively large quantities of foreign metals.

4. The reagent is more specific for copper than any of the other reagents heretofore proposed, and possesses an advantage over the ferrocyanide test in that small quantities of iron do not interfere with its use.

THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES.*

By ROGER C. WELLS.

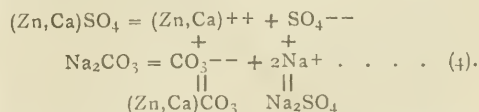
(Continued from p. 171).

CARBONATES (continued).

Experiments with Carbonates at Ordinary Temperature.

IN making fractional precipitations of carbonates two metallic salts were precipitated by less than their chemical equivalent of soluble carbonate, and the ratio of the metals in the precipitate determined.

The first precipitations were made in flasks which stood at the temperature of the laboratory, and were shaken from time to time. The analyses were carried out by difference; that is, by analysing an aliquot part of the solution after filtering off the precipitates and subtracting the quantities found from the quantities taken. The general scheme of this ionisation and reaction in solution may be illustrated by a mixture of zinc sulphate, calcium sulphate, and sodium carbonate as follows:—



Since, in the fairly dilute solutions used, the soluble salt, in this experiment sodium sulphate, plays an insignificant part, the scheme may be simplified even further as follows:—



Information can be gained in the first place by considering what will happen when equivalent quantities of the two metals are present, with just enough carbonate for one, and afterward by noting whether the result so found is changed for other proportions of the metals.

* Bulletin 609, United States Geological Survey.

From Equation 5 it is evident that the equilibrium to be determined may be obtained by precipitating both the metallic salts with a soluble carbonate or by treating a carbonate of one metal with a soluble salt of the other metal. The first method was chiefly used, and the results are presented below.

In these results the radicles and metals are expressed in mgrm. equivalents, an equivalent being equal in mgrms. to the molecular weight of the metal or radicle reduced to a univalent basis. The solution was made up to 1 litre in every experiment, or was calculated to that basis.

Preliminary Results of Experiments with Carbonates at 25° C., with Equivalent Quantities of Two Metals Present and Carbonate enough for One.

Quantity taken (mgrm. equivalents).		Quantity precipitated (mgrm. equivalents).	
Experiment 4. (Time, seventeen days)—			
ZnSO ₄	8.0	Zinc	6.52
CaSO ₄	8.0	Calcium	None
Na ₂ CO ₃	8.0		
Experiment 5. (Time, nineteen days)—			
CdSO ₄	20.0	Cadmium	15.5
ZnSO ₄	20.0	Zinc	4.5
Na ₂ CO ₃	20.0		
Experiment 6. (Time, three days)—			
FeSO ₄	10.0	Iron	6.25
CaSO ₄	10.0	Calcium	None
Na ₂ CO ₃	10.0		
Experiment 7. (Time, two days)—			
CuSO ₄	10.0	Copper	5.30
FeSO ₄	10.0	Iron	5.35
Na ₂ CO ₃	10.0		
Experiment 8. (Time, twenty-six days)—			
CuSO ₄	8.0	Copper	6.84
ZnSO ₄	8.0	Zinc	0.76
Na ₂ CO ₃	8.0		

Prescott and Johnson state that calcium carbonate has no action on zinc salts at ordinary temperature ("Qualitative Chemical Analysis," 1903, 5th Ed., p. 179). Since the above experiment shows a considerable precipitation of the zinc—to be exact 6.52 mgrm. equivalents in 8 or 81.5 per cent in seventeen days—it appears that the duration of the experiment is a factor to be considered. This was confirmed by further experiments, in which finely-powdered calcite was introduced into zinc sulphate instead of precipitating the two salts with sodium carbonate.

In one experiment (No. 12) 8 mgrm. equivalents of calcite were introduced into 8 mgrm. equivalents of zinc sulphate in a litre. The flask was shaken occasionally at room temperature. After two days 16.5 per cent of the zinc was precipitated, and after twenty-four days 81.2 per cent was precipitated.

In another experiment (No. 9) precipitated calcium carbonate, which had been previously dried and heated, was digested at 20–25° for three hours with dilute zinc sulphate. No zinc was precipitated. These results show that hasty chemical experiments may lead to greatly mistaken conclusions in geologic investigations. At ordinary temperature several days are required to show the effect, and, in fact, it is not certain that equilibrium was attained in these experiments, but it is certain that calcium carbonate will precipitate considerable zinc in time, even at ordinary temperatures. On the other hand, too long continuation of experiments in glass vessels introduces an uncertainty on account of the slow production of basic salts due to the action of the glass.

The fact that in the first experiment with zinc sodium carbonate was added, whereas in those just mentioned calcite was used, necessitates a consideration of the varieties of calcium carbonate. It is generally true that a freshly precipitated substance is more soluble than the same substance after a lapse of time. With some substances this is due to the size of the particles, with others

to the crystalline form, and these facts must be considered in precipitations with solids. As regards calcium carbonate, W. Meigen (*Naturf. Gesell. Freiburg im Breisgau Ber.*, 1903, Bd., xxx., 64) has shown that when calcium chloride solutions are precipitated by sodium carbonate aragonite separates, in globules at low temperatures, in needles at high temperatures, and that on standing under some conditions this aragonite passes into calcite. Since aragonite is more soluble than calcite, it would be expected to have a slightly greater precipitating power on solutions of metallic salts than calcite. Meigen has shown that this is the case. This study has been continued by his students (L. Gassner, "Weitere Beiträge zur Kenntniss des kohlensauren Kalks," Inaug. Diss., Freiburg im Breisgau, 1906).

Similar conclusions can be drawn from my own experiments with freshly precipitated calcium carbonate. As a variation of the fractionation in one experiment (No. 13), the calcium sulphate was first precipitated with its equivalent of sodium carbonate, then, without filtration, zinc sulphate was added, and in two hours 17.6 per cent of the zinc was precipitated. With the calcium carbonate which had been previously dried and heated no zinc was apparently precipitated, even in three hours, but after twenty-four days the zinc was practically all precipitated.

The conclusion from all the experiments with zinc and calcium at ordinary temperature is that calcium carbonate in any form will ultimately precipitate a considerable amount of zinc from zinc sulphate solutions, but that the metathesis takes time to occur. Moreover, it occurs slowly with well-dried calcium carbonate, more quickly with aragonite than with calcite, and most quickly with freshly precipitated calcium carbonate.

These results immediately suggest new experiments concerning the action of calcium carbonate on salts of iron, aluminium, chromium, cobalt, nickel, and manganese. It is held in qualitative analysis that a suspension of freshly precipitated calcium carbonate will precipitate ferric, aluminium, and chromic salts in the cold, but have no action on ferrous, cobalt, nickel, manganese, and zinc salts. Chromic salts are said to precipitate more slowly than aluminium or ferric salts (A. B. Prescott and O. C. Johnson, "Qualitative Chemical Analysis," 1903, 5th Ed., p. 154).

According to Meigen's researches (*op. cit.*, p. 83), a hundredfold excess of calcite precipitated a 0.045 normal solution of manganese to the extent of 2.9 per cent in seventy-two hours at 17°, and aragonite precipitated 70.2 per cent under the same conditions.

In Experiment 21 calcite was tried with nickel sulphate; 5.10 mgrm. equivalents of nickel sulphate and 4 mgrm. equivalents of sodium sulphate in 500 cc. of water were shaken occasionally with 4 mgrm. equivalents of powdered calcite for seventeen days. The precipitate then showed 0.36 mgrm. equivalents of nickel and 3.89 mgrm. equivalents of calcium. Hence the precipitation of the nickel by calcite after seventeen days was slight, only about 7 per cent of the whole quantity, but Experiment 87 shows that time is an important factor in this action, and that eventually nickel is very largely, if not completely, precipitated.

Magnesium carbonate, like calcium carbonate, is known to exist in several forms which differ in solubility, and which must therefore also differ in their capacity for precipitating other carbonates. The most soluble form is the trihydrate, MgCO₃·3H₂O. A litre of pure water saturated with this salt contains 0.23 grm. of magnesium and 0.42 grm. carbon dioxide at 20°, according to Auerbach (*Zeit. Elektrochem.*, 1904, x., 161), in the absence of any excess of carbon dioxide. I have found its solubility under atmospheric conditions; that is, its solubility in water in equilibrium with air containing the normal amount of carbon dioxide, to be somewhat greater, namely, 0.36 grm. magnesium per litre, total carbon dioxide 1.01 grm. per litre. Amorphous magnesite was found to be much less soluble than this. No experiments were made

Summary of Fractional Precipitations of Carbonates at Ordinary Temperature.

Experiment.	Quantity of mixture taken (mgrm. equivalents per litre).		Duration of experiment (days).	Quantity of the metal found in precipitate (mgrm. equivalents).	
4.	8 ZnSO ₄ ..	8 CaSO ₄ ..	17	6.52 zinc ..	Trace calcium.
5.	20 CdSO ₄ ..	20 ZnSO ₄ ..	19	15.5 cadmium ..	4.5 zinc.
6.	10 FeSO ₄ ..	10 CaSO ₄ ..	3	6.25 iron ..	Trace calcium.
7.	10 CuSO ₄ ..	10 FeSO ₄ ..	2	5.30 copper ..	5.35 iron.
8.	8 CuSO ₄ ..	8 ZnSO ₄ ..	26	6.84 copper ..	0.76 zinc.
22.	8 Pb(NO ₃) ₂ ..	8 AgNO ₃ ..	4	8.00 lead ..	0.08 silver.
23.	8 Pb(NO ₃) ₂ ..	8 Cd(NO ₃) ₂ ..	6	8.00 lead ..	0.42 cadmium.
24.	8 Zn(NO ₃) ₂ ..	8 Pb(NO ₃) ₂ ..	6	7.96 lead ..	Trace zinc.
25.	8 AgNO ₃ ..	8 HgNO ₃ ..	24	2.28 silver ..	7.98 mercury.
26.	8 AgNO ₃ ..	8 Cd(NO ₃) ₂ ..	4	0.30 silver ..	7.18 cadmium.
27.	8 ZnSO ₄ ..	8 NiSO ₄ ..	10	5.00 zinc ..	1.50 nickel.
28.	8 AgNO ₃ ..	8 Zn(NO ₃) ₂ ..	8	1.60 silver ..	3.96 zinc.
29.	8 FeSO ₄ ..	8 NiSO ₄ ..	1	4.20 iron ..	3.06 nickel.
30.	8 FeSO ₄ ..	8 Zn(NO ₃) ₂ ..	1	2.66 iron ..	2.64 zinc.
31.	8 Cd(NO ₃) ₂ ..	8 HgNO ₃ ..	11	3.54 cadmium ..	7.36 mercury.
32.	8 MnSO ₄ ..	8 CaSO ₄ ..	2	6.56 manganese ..	1.61 calcium.
33.	8 NiSO ₄ ..	14.54 MgSO ₄ ..	5	5.94 nickel ..	Trace magnesium.
34.	8 NiSO ₄ ..	8 MnSO ₄ ..	9	4.04 nickel ..	3.80 manganese.
39.	8 AgNO ₃ ..	8 MnSO ₄ ..	7	3.98 nickel ..	5.76 manganese.
41.	8 AgNO ₃ ..	8 CaSO ₄ ..	7	6.80 silver ..	1.56 calcium.
42.	8 CaSO ₄ ..	8 MgSO ₄ ..	8	1.60 calcium ..	1.12 magnesium.
55.	8 HgNO ₃ ..	8 Pb(NO ₃) ₂ ..	6	3.50 mercury ..	0.75 lead.
60.	8 CuSO ₄ ..	8 CdSO ₄ ..	8	7.24 copper ..	0.20 cadmium.
64.	8 NiSO ₄ ..	8 AgNO ₃ ..	6	3.16 nickel ..	2.96 silver.
71.	16 ZnSO ₄ ..	16 MnSO ₄ ..	18 hours	11.96 zinc ..	8.96 manganese.
74.	16 MnSO ₄ ..	16 CaSO ₄ ..	1 hour	14.80 manganese ..	5.70 calcium.
78.	8 ZnSO ₄ ..	8 CdSO ₄ ..	15	1.26 zinc ..	2.34 cadmium.
87.	8 NiSO ₄ ..	8 CaSO ₄ ..	800	7.99 nickel ..	1.80 calcium.
90.	20 Fe(NO ₃) ₂ ..	20 Pb(NO ₃) ₂ ..	1	2.40 iron ..	10.0 lead.
91.	20 Fe(NO ₃) ₂ ..	20 Cu(NO ₃) ₂ ..	1	10.65 iron ..	10.20 copper.
92.	20 FeSO ₄ ..	20 CdSO ₄ ..	1	2.90 iron ..	11.06 cadmium.
93.	20 ZnSO ₄ ..	20 FeSO ₄ ..	1	15.80 zinc ..	4.2 iron.

Precipitation Series deduced from the Experiments on Fractional Precipitation of Carbonates and Relative Precipitation of the Two Metals.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.	Ratio of major to minor constituents.
55.. ..	Mercury	Lead	Large
31.. ..	"	Cadmium	2.1
25.. ..	"	Silver	3.5
59.. ..	Lead	Copper	Large
90.. ..	"	Iron	6.5
23.. ..	"	Cadmium	19.0
24.. ..	"	Zinc	Large
22.. ..	"	Silver	100.0
7, 91 ..	Copper	Iron	1.0
8	"	Zinc	9.0
60.. ..	"	Cadmium	36.0
78.. ..	Cadmium	Zinc	1.9
92.. ..	"	Iron	4.0
67.. ..	"	Nickel	2.8
26.. ..	"	Silver	25.0
28.. ..	Zinc	"	2.5
27.. ..	"	Nickel	3.3
4	"	Calcium	6.5
71.. ..	"	Manganese	1.3
93.. ..	"	Iron	3.7
7	Iron	Copper	1.0
30.. ..	"	Zinc	1.0
29.. ..	"	Nickel	1.4
6	"	Calcium	6.3
34.. ..	Nickel	Manganese	1.7
33.. ..	"	Magnesium	Large
87.. ..	"	Calcium	"
64.. ..	"	Silver	1.1
32, 74 ..	Manganese	Calcium	4.0
41.. ..	Silver	"	4.4
42.. ..	Calcium	Magnesium	1.4

with crystallised magnesite, which is rather difficult to obtain.

Other fractional experiments were made, beginning with Experiment 22, the results of which, together with the preceding experiments, are shown in the table, all results corresponding to a volume of 1 litre. In most experiments 8 mgrm. equivalents of sodium carbonate were used, but a few variations were made as follows:—Experiment 32, 10.28; Experiment 34, 8.80; Experiment 39, 8.30; Experiments 71 and 74, 16 mgrm. equivalents of sodium carbonate.

The results show that very rarely was a complete separation effected in the fractionation in the time allowed; in most of the experiments both metals were found in the precipitate and filtrate. The separations are far less sharp than those obtained with sulphides. The precipitation series deduced from these experiments is shown in the table below. The numbers in the third column indicate the ratio, in equivalents, of the predominating metal to the one in smaller amount in the precipitate. Not all the experiments have been made which could be made; conversely some of the orienting experiments were later seen to show little except that the two metals were widely separated in the series.

Incidental to the determination of relative solubility the experiments showed that metallic silver was precipitated with ferrous and manganous salts, and there was also a very slight darkening of the precipitate with nickelous salt. The exact position of silver is therefore in some doubt, but it is certainly below zinc.

The positions of manganese and nickel are inconsistent with the recorded solubilities. Either the solubility of manganese carbonate should be less than that of calcium carbonate or there was oxidation of the manganese salt in Experiment 70. Nickel shows a similar discrepancy.

The experiments further throw doubt on the solubility of ferrous carbonate given on page 171, although it must be

said that the fractionations with ferrous sulphate were not very satisfactory. The difficulty was partly due to the ready oxidisability of ferrous sulphate and partly to the apparent tendency of iron to enter into double compounds containing an atom of iron to one of the other metal. There is also a tendency toward the formation of bicarbonates, which is considered later on.

The heats of precipitation for the metallic carbonates are so small that no apparent regularity exists in the relation between the heats and the positions in the precipitation series.

(To be continued).

THE INTERNATIONAL MOVEMENT OF CHEMICAL MANURES DURING THE SECOND HALF AND THE WHOLE OF THE YEAR 1915.

UNDER the above title the International Institute of Agriculture, Rome, has just published in the *International Crop Report and Agricultural Statistics* its half-yearly review on the production, commerce, and prices of manures and chemical products useful to agriculture. The most important information of the review is summarised or reproduced in the following:—

I. World's Production.

Regarding *natural phosphates*, the particular conditions of the industry, on account of the international situation, have diminished the amount of data available for the years 1914 and 1915. On the other hand, the cost of maritime transport has attracted attention to the international movement of this product, especially so far as ocean shipments are concerned.

The available data for producing countries are as follows (in metric tons):—

	1913.	1914.	1915.
United States—			
Production (3 principal states) ..	3,141,750	2,626,085	—
Shipments from Florida ..	1,922,954	1,604,289	906,933
Tunis—			
Total production ..	2,284,678	1,443,767	1,389,074
Shipments ..	1,984,880	1,427,161	1,100,000

The only data available on *basic slag* are those for Great Britain and Ireland, which produced 392,194 tons in 1914 and 386,098 in 1915.

For *nitrate of soda* the circumstances also impeded at first not only shipments and deliveries but also production, but the latter now shows a very notable improvement in consequence of a great increase in the consumption of nitrate by industrial establishments.

The following is a summary of the nitrate of soda movement in the last three years:—

(Metric tons).	1913.	1914.	1915.
Production ..	2,773,552	2,464,427	1,763,639
Exports ..	2,739,530	1,847,586	2,031,338
Deliveries for consumption ..	2,556,973	2,248,976	860,825 (a)
Visible stocks (Dec. 31) ..	1,772,161	1,199,078 (a)	991,394 (a)

(a) Incomplete data owing to the circumstances.

For *sulphate of ammonia*, of which the principal data available to the public are given hereby, it may be noted that the quantities left for agriculture are less important than usual on account of the needs of industrial establishments.

(Metric tons).	1913.	1914.	1915.
Germany (sales) ..	335,232	413,837	—
France (production) ..	75,400	91,500 (a)	42,000
Great Britain (production) ..	438,930	433,235	429,768
Italy ..	13,428	14,323	15,000
United States ..	176,901	166,015	192,323

(a) Consumption.

The same observations hold good for synthetic nitrogenous manures, such as *calcium cyanamide*, of which the productive capacity of factories considerably increased since 1913, both through extensions and through the construction of new factories, as will be seen from the following table on productive capacities:—

(Metric tons).	1913.	1914.	1915.
Germany ..	24,000	36,000	—
Austria-Hungary ..	7,500	24,000	—
Italy ..	14,980	30,000	30,000
Norway ..	22,100	69,000	69,000
North America ..	48,000	64,000	64,000
Japan ..	7,000	7,500	24,000

For *sulphur*, also, a commercial depression and a diminution in production in Italy is to be noted while the United States shows an increased production.

Sulphate of Copper.—The outstanding characteristic in the past season and in the current one for this product is the impossibility for local supply to meet the demand at suitable prices, an impossibility compensated with difficulty by the imports, below normal, from the chief producing countries, Great Britain and the United States.

II. International Commerce.

For almost all the manures and chemical products useful to agriculture the great decreases in imports and exports, already indicated in the preceding half-yearly review, continue. In addition, several European countries no longer publish the figures for their foreign commerce, and therefore cannot be considered.

For other countries the most notable diminutions are as follows, among countries having the most important trade:—

(Metric tons).	1913.	1914.	1915.
<i>Natural Phosphates.</i>			
France (imports) ..	940,791	661,429	325,114
Japan (imports) ..	331,288	285,097	135,800
United States (exports) ..	1,388,452	979,585	206,019 (a)
Tunis (exports) ..	1,984,880	1,427,161	1,100,000

(Metric tons).	1913.	1914.	1915.
<i>Basic Slag.</i>			
Great Britain (imports) ..	51,954	16,838	—
Italy (imports) ..	119,257	23,224	1,180 (a)
Russia (imports) ..	186,410	118,495	3,260 (a)

(Metric tons).	1913.	1914.	1915.
<i>Superphosphate.</i>			
Spain (imports) ..	150,235	116,897	63,013
France (imports) ..	100,822	58,155	14,038
Russia (imports) ..	196,851	122,239	33 (a)

(Metric tons).	1913.	1914.	1915.
<i>Potash Salt.</i>			
United States (imports) ..	957,361	714,088	71,337 (a)

(Metric tons).	1913.	1914.	1915.
<i>Sulphate of Ammonia.</i>			
Japan (imports) ..	111,520	105,632	19,949

(Metric tons).	1913.	1914.	1915.
<i>Sulphur.</i>			
France (imports) ..	186,344	115,782	99,396

(Metric tons).	1913.	1914.	1915.
<i>Sulphate of Copper.</i>			
Italy (imports) ..	30,450	21,906	13,840 (a)

(a) Data incomplete.

Only *nitrate of soda* in the last two years shows figures well sustained in comparison with 1913.

III. Wholesale Prices.

All the manures and products with which we are dealing at present continued during the second half of 1915, except phosphates, for which the rates remain practically unchanged, to increase constantly in price. At the beginning of 1916, however, there was a certain slowing down in this constant rise, and sometimes even a stop, if not a falling back.

The prices of the principal products on the chief markets at the beginning and at the end of the second half of 1915 and at the beginning of 1916 were:—

(Gold francs per metric quintal).	Beginning. Second half. 1915.	End. Second half. 1915.	Middle. First three months. 1916.
<i>Nitrate of Soda.</i>			
French Atlantic ports	34'26	37'35	37'35
Genoa	37'40	47'35	38'83
Liverpool	30'41	37'86	43'07
New York	28'61	38'25	42'79

<i>Sulphate of Ammonia.</i>			
Paris	39'97	47'87	49'15
Hull	36'46	42'82	47'16
New York	41'51	47'11	45'71

<i>Sulphate of Copper.</i>			
French Atlantic ports	73'76	109'88	107'32
London	67'34	109'85	115'43
Genoa	96'50 (a)	142'50	142'50
New York	86'24	149'72	239'03

(a) End of October, 1915.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 6, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Instability of the Pear-shaped Figure of Equilibrium of a Rotating Mass of Liquid.*" By J. H. JEANS.

"*A Hypothesis of Molecular Configuration in Three Dimensions of Space.*" By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

"*Motion of Solids in a Liquid Possessing Vorticity.*" By J. PROUDMAN.

"*The Ultra-violet Absorption Spectra of Blood Sera.*" By S. J. LEWIS, D.Sc.

The work described in this preliminary paper has for its object the investigation of the absorption spectra of blood sera in the ultra-violet region of the spectrum. Modern spectrophotometers are used to determine the absorption values on passing ultra-violet light through a prescribed layer or solution of serum. With these values as ordinates and wave-lengths as abscissæ an absorption curve is drawn. With normal serum the general characters of the curve are constant, and these is very little variation in detail. With certain pathological sera the curves show much greater modifications, and some of these are well defined and appear to be peculiar to given diseases. It was found that the major part of the absorption is due to the proteins.

"*The Growth-rings on Herring Scales.*" By G. W. PAGET, B.A., and R. E. SAVAGE.

SOCIETY OF CHEMICAL INDUSTRY (LONDON SECTION).

Ordinary Meeting, April 3, 1916.

"*The Federation of the Interests of Applied and Pure Chemistry in an Imperial Union of bodies representing the various branches.*" By HENRY E. ARMSTRONG, F.R.S.

The author pointed out that to bring about more the effective co-operation of all the interests that may properly be collected under a chemical banner, it was desirable to establish in the immediate future an Imperial Union or Institute of chemical science and industry—an Imperial Society of Chemistry, scientific and industrial. An example was to be found in the Royal Society of Medicine. In 1817, seventeen societies, representing various sections of the scientific activities of medical men, were dissolved, and their members admitted as members of the Royal Medical and Chirurgical Society, which was granted an enlarged charter for the purpose. It was desirable to effect a similar union in the interests of chemistry throughout the Empire. Chemical Societies generally, scientific and industrial, should be included with sub-sections, if found desirable for agricultural chemistry, chemistry of fuel, metallurgy, ferrous and non-ferrous, chemistry in relation to brewing and distilling, dyeing, the textile trades, analytical, physical, biological, and photographic chemistry. Sections should be maintained in outlying parts of the Empire, and, if desirable, in provincial towns. A house in London should be the headquarters, with ample space for meetings and a common library. Possibly a club might form part of the proposal. There would be issue of transactions and a weekly journal, with full information and abstracts. Much more complete and efficient organisation of literary effort than now existed was required to bring the science into repute and to make it of avail to chemists themselves.

DISCUSSION.

Mr. A. CHASTON CHAPMAN, while expressing himself in sympathy with Prof. Armstrong's suggestion, pointed out that there was a difference between chemists and medical men. Medical men, whether specialists on any given branch, had all received the same kind of training, which was not the case with the members of the different chemical societies. Again, he thought that the chemical societies, which were well established, might fear losing much of their individuality by federating in the manner suggested. He thought that the General Committee appointed by the Chemical Society, which consisted of members of various other societies, should have this suggestion put before them.

Dr. L. T. THORNE thought that at this critical time some form of federation of chemical societies was needful if we were to regain our chemical industries. The separation of pure and applied science had been harmful, and the Society of Chemical Industry might make an effort in the direction indicated.

Dr. DUNN said that Mr. Chapman pointed out certain obstacles in the way of Prof. Armstrong's suggestion, but he thought that the desirability of carrying out this federation was so great that the obstacles would of necessity be overcome. He thought that it was time to look into the question of the publication and co-ordination of abstracts, and he also considered that the formation of a chemical club in London, at which those from the provinces who visited the metropolis at intervals might meet their chemical friends, was desirable.

The President (Dr. C. CARPENTER) said that Prof. Armstrong's suggestion was a fascinating one, and in ordinary times there would be no difficulty in bringing all connected with chemistry together. The desirability of such a scheme was undoubted. During these abnormal times, however, he feared there would be a difficulty in launching it.

Prof. PHILIP said that he thought that the sub-division in various branches of chemistry which obtained at the

present time was a natural process, and that there would be even more specialisation in the future. There were cases in which interests to be served differed, and such points as this could be settled by a Joint Committee.

Mr. GARDNER said he hoped that this matter would not be brought before the General Committee, as suggested by Mr. Chapman, but that it would be put before individual members of the Society.

Mr. BUTTERFIELD said that the analogy to the chemists should have been taken from the engineering rather than the medical profession. There were a number of societies in the engineering profession which looked after a special branch of work. In fact, the tendency was rather towards subdivision. As to headquarters of the federated society, he thought that the Institute of Chemistry had now a building which was rather larger than was required for its immediate purposes, and if that Institute would in some way open its doors to the members of the profession who were not Fellows of the Institute, that building might well afford a good meeting ground for chemists in general.

Mr. HINCHLEY said that he believed chemists were suffering not from lack of organisation, but from lack of emulation. The societies had at the present time enough organisation, but not of the right sort. They wanted organisation to produce emulation, and to make every member feel sure that he had a stake in the society and in the country of which the Society was a part.

Mr. CARR said that the difficulty due to the individualities and feelings of jealousy would disappear by reason of the fact that the one great need was the need of subdivision.

Mr. MAYBURN, speaking as a member of the Royal Society of Medicine, said that he wished to say that he was quite sure that Society would be delighted to entertain the Society of Chemical Industry at their house in Wimpole Street. In the case of the Royal Society of Medicine, Mr. Macalister, their Secretary, was the man who had carried their own scheme through successfully, and what was needed was such a man to launch the suggested scheme.

The CHAIRMAN said that they had had a very useful discussion and were all in agreement with Prof. Armstrong's suggestion if it could be carried out. He himself thought it could be carried out, and, as Prof. Armstrong had said, if they missed the present opportunity it would not recur. It was on account of the specialisation of their chemical work that they needed to be brought together so that specialists might see what those in other branches of chemistry were doing. He was very much attached to the Society of Chemical Industry and many others, but could not help thinking that societies were often run for their own sake rather than for their objective, the development of science.

Prof. ARMSTRONG, in reply, said that his object was to make chemistry a living agency in this country, which at the present time it was not, and he put it to the meeting and to those who read the discussion later on, that unless chemists were very careful, and if they went on in the way they were going at the present time throughout the country, at the end of it they would have no position at all. He was not in agreement with Mr. Chapman's suggestion that the matter should be put in the hands of the General Committee of the Chemical Society. In his opinion it must be given into the hands of the younger members of the Society, and put through as a democratic movement if treated at all. If the younger men would come forward and have a little courage something might be done, and he urged them to form a Sub-Committee.

"A Comparison of the Brazilian and Plantation Methods of Preparing Para Rubber." By G. STAFFORD WHITBY, Chemist to the Society Financiere des Caoutchoucs.

In order to obtain strictly comparable results, the two methods were applied to separate portions of the same lot of freshly-tapped latex. The Brazilian method

employed for the preparation of the fine hard Para rubber was followed as closely as possible, the latex being coagulated on a paddle in smoke from burning rubber, wood, and atap palm nuts. The plantation method adopted as typical was the preparation of smoked sheet by oiling the latex, coagulating it with acetic acid (0.5 per cent of the weight of dried rubber), rolling out the coagulum, drying the sheets, and finally hanging them in a smoke-house for twenty-two days. The products obtained by these two methods were subjected to precisely similar vulcanisation tests, the results of which were expressed in accordance with a scheme worked out by P. Schidrowitz (see "The Rubber Industry," London, 1914, p. 212 *et seq.*) to indicate the duration of heating required for a "perfect" cure and the mechanical properties of the vulcanised product. The results indicate that the Brazilian method is not superior to the plantation method, and the rubber coagulated by the Brazilian method required longer curing in the vulcanisation tests. Such differences as were observed the author attributes in part to a specific and deleterious action of phenolic substances derived from the smoke, and the presence of formaldehyde may also be responsible to some extent. From vulcanisation tests on a very large number of samples, the author concludes that oxidation and the discoloration which it produces have no effect on the vulcanising properties of rubber; the outer and more discolored portions of balls of fine hard Para rubber were found to be equal in quality to the inner portions. Separate investigation of rubber from young and from old trees gave no support to the widely accepted opinion that the latex from young trees is inferior. In further experiments it was ascertained that air-dried plantation sheet rubber is quite equal if not superior in quality to smoked sheet rubber.

DISCUSSION.

Prof. ARMSTRONG said that the impression he had formed when recently in Ceylon was that they practically understood very little of what they were doing, and that more research work was necessary in regard to rubber than was being practised at the present time.

Dr. STEVENS said that for some years there had been research stations in Ceylon and Malaya, and rubber stations had been carrying out work for some six or seven years past, and researches had also been carried out at the Imperial Institute and private laboratories.

Mr. PELLEY said that about three years ago a large number of Ceylon planters had got together, found the money, and devised a scheme to be worked under the Imperial Institute to better, if possible, the methods of obtaining plantation rubber. Samples had been sent to the Imperial Institute, and had been tested by Mr. Whitby, Mr. Eaton, Dr. Stevens, and others.

Prof. ARMSTRONG thought Dr. Stevens was quite right in his criticism, but the question was whether the Brazilian method of smoking had been successfully innovated. In the sense in which he meant it, there was no research work going on. The men there were just able to keep the machine running and that was all.

(NEW YORK SECTION).

THE last meeting of the Section was held on Friday, March 24, 1916.

The programme for the evening was:—

"The Development of Low Expansion Glasses." By E. C. SULLIVAN.

The glass, aside from low expansion, must be highly resistant to attack by moisture and other reagents; it must be meltable and workable, it must not crystallise, it must have suitable tensile strength and elasticity, and it should be transparent. It is the glassmaker's problem to unite these qualities in one glass. Methods used for measuring some of these properties are described. Development is sketched from stable glasses of comparatively high expansion through unstable glasses of low expansion to glasses

having both low expansion and high stability. As a container for material to be heated by means of radiated heat, glass has the advantage over metal that it reflects only about 10 per cent of the energy, while metal reflects up to 90 per cent or more. The low expansion glass shows good mechanical strength as compared with earthenware and crockery.

"The American Pressed and Blown Glass Tableware Industry." By S. R. SCHOLES.

A brief mention is made of the development of the art, the technology of the industry, describing the pots and furnaces and the melting process, the operations of gathering and pressing, a description of annealing lehrs and kilns, selecting ware, cutting and polishing, operations of gathering and blowing, pulling stems and foot-setting, finishing blown ware. These processes illustrated by photographic slides. The chemistry involved, with special reference to decolorising. A discussion of disadvantages in using manganese as a decoloriser, the behaviour of manganese in the glass, and a new theory for the "burning out" of the manganese colour. The theory proposed is that the manganese goes into new forms of combination, such as manganites or manganates, that have a green colour. Suggested substitutes for manganese. Specimens of ware in various stages of manufacture are shown, and exhibits illustrating the behaviour of manganese during the melt and in special kinds of glass.

"Glass we see Through." By G. OSGOOD ANDREWS.

The importance and usefulness of glass, the history and development of glass manufacture, methods of making window glass, methods of making plate-glass, general conditions covering the glass industry, American made glass as compared with foreign glass.

MISCELLANEOUS.

Sir William and Lady Crookes have this week celebrated their diamond wedding, and I am sure many South Africans will wish the great scientist and his good lady many happy returns of the day. Sir William is well known in Kimberley, where, if I remember aright, he showed them how to make a diamond. I know he once manufactured diamonds in full view of an audience at the Royal Institution, so it is quite fitting that he should reach his diamond wedding day.—*South Africa*, April 15, 1916.

The Neglect of Science.—The Meeting called by the Committee for May 3 will be held at Three o'clock in the afternoon at the Rooms of the Linnæan Society, Burlington House, Piccadilly. The following Resolutions will be submitted to the meeting:—

- (1) That in the opinion of this meeting it is a matter of urgency, in order to promote national efficiency in the near future, that the natural sciences should be made an integral part of the educational course in all the great Schools of this country, and should form part of the entrance examination of the Universities of Oxford and Cambridge as well as of the newer Universities.
- (2) That it is in the highest degree desirable that the Government should exercise the large power which it possesses of encouraging the study of the natural sciences, and thereby increasing the efficiency of our public servants (1) by assigning capital importance to the natural sciences in the competitive examinations for the Home and Indian Civil Service; (2) by requiring some knowledge of the natural sciences from all candidates for admission to Sandhurst.
- (3) That this meeting is of the opinion that the method indicated in Resolution 2 is the only one by which it is practicable to bring about the desired change in the attitude of the Schools and Colleges throughout the country towards the natural sciences and to make some knowledge and understanding of those

sciences general. As the results of such changes will only develop in the course of years, it is urgent that the matter should be at once taken in hand by His Majesty's Government.

- (4) That the Committee are authorised to take such steps as they may consider appropriate in order to bring these views to the notice of His Majesty's Government.

Among those expected to speak in support of these resolutions, besides some of the signatories of the original Memorandum on "The Neglect of Science," are Lord Montagu of Beaulieu, the Right Hon. Arthur Dyke-Acland, the Right Hon. F. Huth Jackson, Sir H. H. Johnston, G.C.M.G., Sir Hugh Bell, Bart., Mr. H. G. Wells, Mr. Nowell Smith of Sherborne, and representatives of the great technical institutes and associations.—E. RAY LANKESTER, Chairman.

Iron and Steel Institute.—Annual Meeting, 1916.—The Annual Meeting of the Institute will be held, by kind permission, in the House of the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 4 and 5, 1916, commencing on Thursday at 10.30 a.m. and on Friday at 10 a.m. The following is the programme of Proceedings:—

Thursday, May 4 (at 10.30 a.m.).

General Meeting of Members.

The Council will present their Report for the year 1915. The Hon. Treasurer will present the Statement of Accounts for 1915.

Scrutineers will be appointed for the examination of Voting Papers for election of new Members of the Institute.

The Acting President will move the adoption of the proposed new By-laws, as amended at the Autumn Meeting, for incorporation in the By-laws of the Institute.

The Acting President (Mr. Arthur Cooper) will induct into the Chair the President-elect (Sir William Beardmore).

The Bessemer Gold Medal for 1916 will be presented to Mr. F. W. Harbord, F.I.C.

The President will deliver his Inaugural Address.

A selection of Papers will be read and discussed.

Friday May 5 (at 10 a.m.).

General Meeting of Members.

The award of grants from the Andrew Carnegie Research Fund in aid of research work will be announced.

Papers will be read and discussed. Those papers for which time cannot be found will be taken as read and discussed by correspondence. After the Presidential Address the following list of papers is expected to be submitted for reading and discussion:—

"Notes on the Theory of the Corrosion of Steel," by L. Aitchison.

"Notes on the Relations between the Cutting Efficiencies of Tool Steels and their Brinell or Scleroscope of Hardnesses," by J. O. Arnold.

"A New Thermo-electric Method of Studying Allotropic Changes in Iron or other Metals," by C. Benedicks.

"Initial Temperature and Critical Cooling Velocities of a Chromium Steel," by C. A. Edwards.

"The Influence of Carbon and Manganese upon the Corrosion of Iron and Steel," by Sir Robert Hadfield and J. N. Friend.

"Early Experiments on the Recalescence of Iron and Steel," by A. Mallock.

"A Few Experiments on the Hardness Testing of Mild Steel," by W. N. Thomas.

"Surface Tension Effects in the Intercrystalline Cement in Metals and the Elastic Limit," by F. C. Thompson.

Autumn Meeting.

The Autumn Meeting will be held, by kind permission of the Council of the Institution of Civil Engineers, at the rooms of that Institution on Thursday and Friday, September 21 and 22.

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THE CHEMICAL NEWS.

VOL. CXIII., No. 2944.

THE USE OF OZONE FOR CHEMICAL RESEARCH AND INDUSTRIES.

OZONE is a powerful oxidising agent which exists in small quantities in nature, but can be produced artificially to an extent only limited by space and money. So far as the British Empire is concerned Ozone may generally be said to be known to chemists but not recognised. It is the Cinderella of the chemical profession and trade, who (with few exceptions) have been content to ignore it as a practical commercial oxidising agent and to regard its suggested applications as the proposals of cranks. The causes for this attitude are not far to seek; in the first place one must take into account the economic status of the British analytical or industrial chemist as it has existed up to the time of the war; in the second place, very few chemists know much or have been able to acquire information about the electrical production of Ozone, its estimation or its practical uses. Much has been written in the daily Press regarding the status of chemists and their training, and although these are questions outside the sphere of this article, they have an important bearing on the subject from the utilitarian and national points of view.

To our shame it must be said that whilst most of the research work in connection with the practical application of Ozone in chemical industries has been done by a British firm, as usual it is the German chemists and manufacturers (often synonymous terms) who have had the enterprise to make practical use of Ozone, and by so-called "secret" processes to flood the markets of the world with certain articles of a better quality than could be obtained in this country. The attitude of the manufacturer here has often been too much in the direction of shying at the capital outlay for an Ozone plant without considering how quickly this may be redeemed by the saving effected in the process. Propositions involving the repayment in two years of the capital sunk have been "turned down" as too expensive, whereas to the men of business they would be termed highly profitable investments. In other cases the status of the works chemist has proved an insuperable barrier to the introduction of any new process by an outside firm. Probably these are some of the things that the war will change, and there are already signs of awakening interest in improved processes in general and in Ozone in particular. The object of this article, therefore, is to stimulate this interest by a general survey of the applications of Ozone to the chemical industry, and to describe some of the Ozone research apparatus and industrial plants which have been evolved as the result of many years' experience.

Applications of Ozone.

Although all chemical applications of Ozone are in the nature of oxidation they may be classified for convenience as follows:—

- (1) Manufacture of chemical preparations by Ozone.
- (2) Treatment of oils, fats, and waxes, and similar substances by Ozone.
 - (a) Bleaching.
 - (b) Deodorising.
 - (c) Refining.
 - (d) Technical oxidising.

In addition to these there are other applications which, although oxidation processes, are actually employed in the course of manufacture of goods. These processes include drying of linoleum, fishing nets, waterproof materials, printed matter, varnished or painted articles, &c.,

bleaching of textiles, maturation of timber, tobacco, wine and spirits, curing of leather, bleaching of sugar and molasses, &c., &c.

Although of interest to chemists, and especially to works chemists, these treatments cannot be discussed within the scope of this article, as they each necessitate apparatus of a special nature, differing considerably from the plants which will be afterwards described, and which have been standardised for the strictly chemical applications of Ozone.

(1) Manufacture of Chemical Preparations by Ozone.

Ozone can frequently replace other oxidising agents with advantage, giving better, cheaper, and quicker results in the manufacture of many of the more expensive chemicals, such as certain synthetic perfumes and aniline dyes and disinfectants. Among these processes may be noted the preparation of vanillin from isoeugenol, heliotropine from isosafrol, artificial hawthorn from amethol, the oxidation of camphene to camphor, the production of indigo from indol, and the manufacture of iodoform from alcohol and iodide of potassium. Ozone has recently also proved to be of value in the oxidation of impurities in tar oil, the conversion of ferrous into ferric salts, and the production of ozonised petrol for internal combustion engines.

Another field, to which attention may be directed at the present moment, is the use of Ozone in dyeing, for fully developing certain colours and producing or modifying others.

A great deal more work still requires to be done in these directions by practical chemists who have the time or by chemical manufacturers who will place at the disposal of their chemists research apparatus such as are described later. It is only by taking up an investigation of this kind (which has been proved in the laboratory) and working it out systematically on a larger scale that practical commercial results can be obtained and present processes superseded by better ones.

(2) Treatment of Oils, Fats, and Waxes, and similar substances by Ozone.

The processes involved in bleaching, deodorising, refining, and technical oxidising are allied to one another, and in fact in many cases two or even three of the processes may be effected by a single treatment. They all more or less rely for their success on the powerful oxidising influence possessed by Ozone.

The object of bleaching is of course to remove natural colouring matter, such as the green vegetable colour (chlorophyll) and the reddish brown colour of palm oil, or of colours due to age or impurities, such as the dark colour of greases, without injuring or altering the composition or nature of the substance bleached.

Liquids may be bleached by various physical methods, such as the use of coagulants, charcoal, or Fuller's earth, but chemical processes alone have to be employed for the bleaching of solid substances. These processes may be divided broadly into two classes: (1) Reduction and (2) Oxidation. The former is entirely an artificial process, and requires the use of such reagents as hydrogen, sulphur dioxide, sulphurous acid (produced by burning sulphur), hydrosulphites, or sulfoxalates. The latter process, on the other hand, is constantly taking place in nature, the oxidising agent being the oxygen in the atmosphere, the action of which is accelerated by sunlight and by moisture, e.g., dew.

Many chemicals have been proposed and used for assisting this natural oxidation, such as potassium bichromate, potassium permanganate, manganese dioxide, bleaching powder, persulphates, perborates, sodium peroxide, hydrogen peroxide, and various organic peroxides. Most of these are open to objection for certain purposes. Thus for the bleaching of food-stuffs it is obvious that no poisonous material should be used; in the bleaching of textiles by means of bleaching powder the chlorine liberated tends to weaken the fibres; sodium peroxide is liable

to explode when in contact with organic matter. In addition most of these "per" salts are very expensive.

(a) *Bleaching*.—The use of Ozone overcomes these difficulties with most substances, and in addition the resultant bleach is much more likely to be permanent than that obtained by reduction, since the natural tendency is for the body to become oxidised on exposure to air. Substances which bleach most readily and efficiently with Ozone are most—

Edible fats and oils,
Soap-making materials,
Industrial oils,
Waxes.

The first include margarine and nut-butter and various animal and vegetable fats, such as tallow, lard, palm oil, coconut and palm kernel oils, and "stearines," cacao butter and other so-called chocolate fats—*e.g.*, Borneo tallow, Illipe fat, Dika fat, &c.

The fact that these are intended for internal consumption precludes the use of practically all the usual chemical bleaching agents, as not only is there, of course, great objection to the use of anything of a poisonous nature for the purpose, but also because some processes, particularly those involving the use of mineral acids, tend to spoil the flavour of the oil. Ozone, however, is free from both of these objections, and, indeed, in some cases rather improves the flavour by the removal of impurities, so that it can be very advantageously used for bleaching.

The same remarks apply to salad oils, olive oils, arachis oils, and monkey nut oil, cotton-seed oil, soya bean oil, turnip-seed oil, and rape oil, &c., all of which may be more or less satisfactorily bleached by the use of Ozone.

As regards soap-making materials, Ozone is a very useful bleaching agent in this industry, doing all that the ordinary oxidation methods will accomplish, but more quickly and effectively and at less cost. The better qualities of palm oil, for example, can be bleached perfectly at a cost of about 2s. 6d. per ton, while the so-called unbleachable palm oils, such as Congo or Salt Pond, are very considerably improved in colour. Tallow, bone fat, and greases are also very readily bleached by treatment with Ozone. Another method of utilising the bleaching effects of Ozone in the soap works is to ozonise the contents of the pan or kettle during the primary saponification or pasting stage, whereby the saponification process is said to be accelerated.

Industrial oils—that is oils used for paints and varnishes—readily combine with Ozone on account of the larger amount of unsaturated bodies which oils of this class, such as linseed oil, contain. In addition to being bleached by the oxidation of the colouring matter, which is an advantage in connection with the mixing of light colours in the paint and varnish industry, they further absorb a considerable quantity of Ozone, which should accelerate the subsequent drying of the paint.

Many waxes can readily be bleached with Ozone. Beeswax, which is probably the most important of the waxes, can be much more rapidly bleached by Ozone than by the ordinary method of air bleaching. Other waxes for which the Ozone treatment is suitable are Carnuba, Insect or Chinese, and Japan waxes.

(b) *Deodorising*.—The offensive odour which many substances possess is due in most cases to organic matter in a state of decomposition with which they are always more or less associated. This is best illustrated in the case of sewage greases, fish meal, tallows, bone fats, and such like materials. These substances, if left exposed to the ordinary air, develop nauseous qualities, although one would imagine that the oxidising properties of the atmosphere would at least stay further development. On the other hand, if treated with Ozone they are at once deodorised by reason of the existing organic impurities being oxidised and the cause of putrefaction destroyed. Such substances as oleine and stearine owe their disagreeable odour to chemical causes, but Ozone completely deodor-

ises these also. The use of Ozone is also found to deodorise coconut oils considerably.

(c) *Refining*.—Refining of various substances is necessary for the purpose of preparation for articles of consumption. By refining is implied the removal of the disagreeable natural flavour or taste which is inherent in some of these substances, which may be said to include practically all the edible fats and oils referred to under "(a) Bleaching."

(d) *Technical Oxidising*.—This term is used to discriminate between the several meanings of the word "oxidising" and the thickening or drying process as applied to the industrial drying oils, such as linseed oil. Whilst this renders them unsuitable for soap making it possesses great advantages in the paint and varnish industry, the drying properties of the oils being increased and accelerated, so that there should be considerable scope for the use of Ozone in the production of quick drying paints and varnishes, such as are required by coach-builders, shipbuilders, and other trades, and the preparation of linseed oil as used in the linoleum and waterproofing trades.

As has already been stated, two or three of these processes will sometimes be effected with a single treatment. For instance, edible oils will be bleached and refined at the same time; fats will be bleached and deodorised; oils may be bleached only or bleached and thickened.

Industrial Ozone Plants.

The method of treatment is almost identical, whether for bleaching, deodorising, refining, or oxidising, and the plant used is practically the same, with only slight modifications to suit particular circumstances. Fig. 1 shows a diagrammatical arrangement of such a plant which was made to bleach beeswax. The process is very simple, and consists essentially in forcing ozonised air through the substance, which is contained in a suitable pan or vessel. Various conditions are used to suit various substances or objects to be achieved. According to the nature of the substance the concentration or strength of the ozonised air must be varied, also the quantity of air per unit of material, and the time during which it is subjected to treatment.

The conditions of temperature, &c., have also to be considered, but the process, generally speaking, is in almost all respects identical.

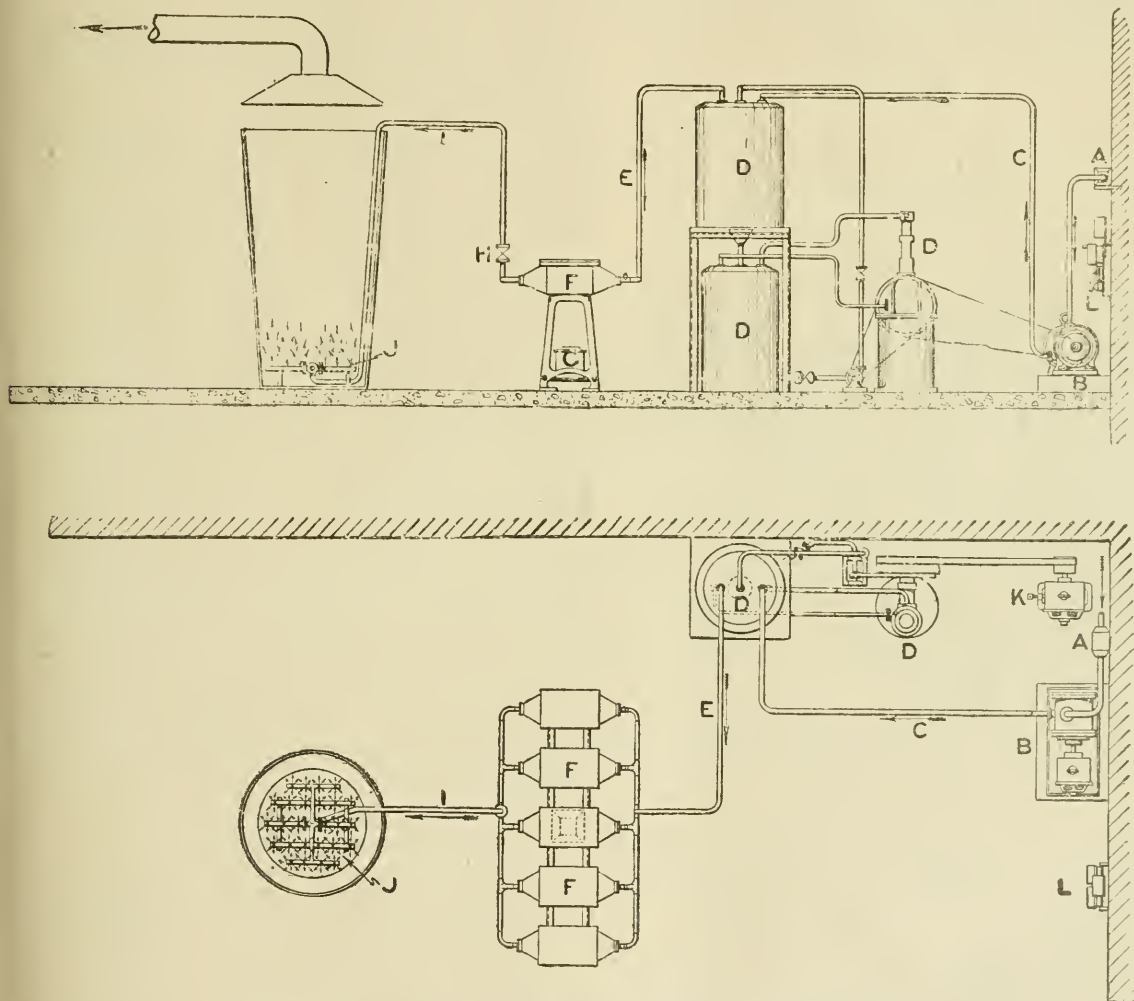
Quite apart from the natural advantages which such a system of treatment has over ordinary chemical processes for such materials as are required for human consumption, this method of bleaching, &c., by Ozone possesses actual commercial value and undoubted merit. In most cases the cost is considerably less, whilst in others the length of time now occupied may be very considerably shortened. In many other cases the results obtained cannot be achieved by any other means.

The plant consists essentially of an electrically driven blower, a refrigerating plant for cooling and drying the air to be ozonised, a battery of Ozone generators, and the vessel in which the material is treated. The blower has a capacity varying with the speed at which it is driven and the resistance of the column of material in the treating vessel.

The air now passes into the cooler of the refrigerating apparatus. This apparatus is worked on the direct expansion system; the temperature of the air issuing from the refrigerating apparatus is about 0° C. The object of this cooling of the air is, firstly, to dry the air by deposition, and, secondly, to cool it, in order to keep the electrodes of the ozonisers cool and thus increase their efficiency.

The air now enters the bank of ozonisers through a series of pipes, which are arranged in order to give an equal volume of air to each ozoniser. The high-tension current is supplied by transformers, whose secondary voltage varies from about 7000 to 9000 volts. This secondary voltage is capable of regulation by means of the

There are still other advantages. In the chemical method of bleaching there is a considerable loss of material, due to the chemical action and to what is



A, Air cleaner; B, Electrically-driven Blower; C, Air Delivery Pipe; D, Air Cooling Machine; K, Electric Motor; E, Cold Air Delivery Pipe; F, Ozone Generators; G, Transformer; H, Valve; I, Ozone Pipe; J, Ozone Injectors; L, Switchboard.

As already stated, the plants, of which the foregoing is a general description, have been standardised for the

strictly chemical applications of Ozone as already defined. For other applications, such as the manufacture of chemical preparations, the industrial plants might differ in various respects, depending entirely on the nature of the substance and the details of the process. The latter has to be worked out in the laboratory, and for this purpose the chemist requires a suitable set of apparatus. He may, firstly, require merely to ascertain whether Ozone will do what he desires, and afterwards, if his results are promising, he will require to make quantitative experiments involving an estimation of the quantity of Ozone used to achieve his end. On the basis of such experiments the chemist may be able to form the necessary conclusions as to whether Ozone will be a more economical reagent for his purpose than the oxidising substances that he used before.

(To be continued).

RECOVERY OF GALLIUM FROM SPELTER IN THE UNITED STATES.

By W. F. HILLEBRAND and J. A. SCHERRER.
Bureau of Standards, Washington, D.C.

SOME months ago a few grms. of gallium of American production were received by one of us (Sherrer) from Mr. F. G. McCutcheon, Chemist of the Bartlesville Zinc Company, Bartlesville, Oklahoma. Recently the other (Hillebrand) received 50 grms. more from Mr. McCutcheon.

The first material contained a little indium and zinc, and a trace of calcium, as determined spectroscopically by Dr. K. Burns at the Bureau of Standards. The second lot is of similar composition, presumably. An as yet incomplete test by one of us (Hillebrand) indicates an indium content probably of less than 1 per cent.

The metal or alloy is a liquid resembling mercury in appearance, but it wets glass and porcelain, and adheres so tenaciously that if agitated in a glass vial the contents can be seen only as a coating on the walls. This latter property is not in evidence if the metal is covered with hydrochloric or sulphuric acid.

Although gallium melts at about 30°, it is said to remain liquid far below this temperature, indefinitely unless inoculated with solid gallium.

Inquiry of Mr. Kurt Stock, Superintendent of the Bartlesville Zinc Company, brought out some exceedingly interesting information, as shown by the following extracts from his letter of reply, dated October 21, 1915:—

"His attention (Mr. McCutcheon's) was drawn to peculiar beads and drops, in appearance like mercury, which seemed to sweat out of zinc-lead dross plates after these had been exposed to the weather for a time. Mr. McCutcheon, with the help of his two assistants, made a great number of tests, proving the material to be an alloy of gallium and indium with small amounts of zinc. . . ."

"Your hope that a new source of supply for both metals has been opened up, with the prospect of continued manufacture, is not shared by me, as the conditions leading to the concentration of gallium and indium are very unusual, and are based on the abnormal state of the spelter market. You are aware that the present demand for high-grade spelter has led zinc smelters to the practice of redistillation, and it is the final leady residue from such continued redistillation that carries gallium in noticeable quantities. . . . We are not at all sure which of the large variety of ores is responsible. Gallium is not found in all dross, and where it is found it does not occur continuously. . . ."

"That the amount in the original ores must be extremely small can well be realised when you consider that the residue from the continued distillation of about 12,000 lbs. of spelter weighs about 60 lbs., and represents our raw material from which we can obtain a few grms. of the

alloys. However, we have at present about 45 tons of dross on hand, which we suspect carries gallium."

"A very interesting feature is that both gallium and indium are volatile at the temperature prevailing in our ore furnaces, where a maximum of 1350° C. is reached for only a few hours, but they resist distillation if kept for three weeks and longer at the temperature at which we operate our redistilling furnaces, namely, about 1000° C."

"Please be assured that we shall leave nothing untried to save these rare metals, but do not get impatient if results are not forthcoming for a while. . . ."

"You may use this very general information any way you desire."

It will be of interest to determine if this metal, hitherto such a rarity, possesses qualities of value in itself or when combined in small amounts with other metals, and if it has such, whether their importance will justify continued production after the price of spelter falls.

So far as known to us, the only uses for gallium that have been so far suggested are in alloy with aluminium as cathode material in metal vapour lamps (T. W. Vogel, *Zentralblatt*, 1910, i., 703; German patent), and for the production of optical mirrors. The fact that it wets quartz would seem to negative the suggestion that it might be suitable in quartz thermometer tubes for measuring temperatures too high for glass instruments. The authors would gladly receive further suggestions.

Also of interest is the particular source of this gallium. Mr. Stock assures us that it comes from domestic ores, probably from certain as yet undetermined ones of Joplin. Its presence has been reported in the past in a number of domestic blends, including one from Joplin. A very recent statement from Mr. Stock is to the effect that the dross produced of late shows no gallium and that the amount of gallium at first thought to be available will not come up to expectations:—"I am more convinced than ever that gallium will remain a rarity, and that a commercial production is out of the question."

Since the foregoing was written, spectroscopic tests have been made at the Bureau of Standards by Dr. K. Burns upon seven samples of zinc ore kindly supplied by Mr. S. M. Rogers, of the American Steel and Wire Company. Germanium was also included in the metals looked for. The data concerning the precise sources of some of the ores tested are unfortunately meagre, particularly with respect to Nos. 2, 4, and 7, but the presumption is strong that No. 4 came from the Joplin district. Of special interest is the fact that this ore showed more of both gallium and germanium than any of the others. The tests obtained by Dr. Burns follow, accompanied by his comments:—

Spectroscopic Tests of Zinc Ores.

No.	Kind and source of ore.	Germanium.	Gallium.
1.	Sulphide—Sunset, Idaho..	Moderate	Moderate
2.	Sulphide—Australia . .	Not found	Moderate
3.	Sulphide—Frisco, Idaho..	Weak	Moderate
4.	Sulphide—Missouri . . .	Strong	Strong
5.	Carbonate — Monarch, Leadville	Absent	Moderate
6.	Carbonate—Doctor Mine, Almont, Colo. . . .	Moderate	Not found
7.	Carbonate—Utah, Nevada	Very weak	Rather weak

"By means of the carbon arc the spectrum was examined in the region 2800 Å to 3600 Å. Large amounts of iron were present in all these samples. This makes the determination of indium by our method not very accurate, as the most sensitive lines of indium coincide either with carbon lines or with iron lines. It is certain, however, that indium is not present in these ores in quantities approaching one-tenth of the gallium found in ores marked 'moderate.'"—*Journal of Industrial and Engineering Chemistry*, viii., No. 3.

THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES.*

By ROGER C. WELLS.

(Continued from p. 188).

CARBONATES (continued).

Results of Experiments with Bicarbonates.

THE effect of basic carbonates on the fractionation and the elimination of this effect will now be considered. If in any precipitation of carbonate a hydroxide of one of the metals possesses such a small solubility that the hydrolysis of the carbonate would result in exceeding the solubility product of the hydroxide, more or less "basic salt" will be formed. These precipitates are ordinarily considered to be indefinite mixtures of hydroxide and carbonate, but it seems highly probable that either a pure carbonate, a hydroxide, or a definite basic salt would result if time were allowed for the attainment of equilibrium, for it has been shown that many days are often required for the attainment of a stable state at ordinary temperatures. This is another instance where the duration of the experiment determines the final product.

It is possible that a basic carbonate of one metal might form at the same time as a bicarbonate of another metal. There is some evidence of this in Experiments 87, 92, and 93. In Experiment 92 the mother-liquor showed 1.1 mgrm. equivalents of HCO_3^- , and in Experiment 93 it showed 5.3 mgrm. equivalents of HCO_3^- per litre.

In order to ensure that carbonates alone are being precipitated the experiments might have been carried out in the presence of a certain excess of carbon dioxide. As a much simpler means to the same end, however, a number of experiments were made with sodium bicarbonate as precipitating agent. The only difficulty encountered in this procedure was the rather large solubility of the bicarbonates of certain metals. The experiments were as given in the table (see next column).

From these results it appears that when bicarbonates are used instead of carbonates the principal changes are that ferrous iron, zinc, and nickel fall below silver in the series.

Experiments with Carbonates at Higher Temperatures.

At 100° C. bicarbonates are no longer stable at low pressures, although the last traces of carbon dioxide are held very tenaciously by solutions containing calcium or magnesium salts. Under high pressures of carbon dioxide and at elevated temperatures the bicarbonates would no doubt persist. The compounds stable under these conditions, however, and their solubilities remain to be determined. A few solubilities have been measured in solutions saturated with carbon dioxide at a pressure of a few atmospheres, but mostly at ordinary temperatures. The crystallisation of dolomite at 150° C. has been noted. Of course many of the metallic carbonates become basic as the temperature rises, as has already been stated, and some lose carbon dioxide on boiling. Hence in most of the experiments the precipitation was made cold, and the flask and contents then heated to 60–80° C.

In Experiment 16 a solution containing 5.43 mgrm. equivalents of cadmium sulphate and 5.43 mgrm. equivalents of zinc sulphate was precipitated with 5.43 mgrm. equivalents of sodium carbonate in a volume of 250 cc. After boiling three hours the precipitate contained 4.76 mgrm. equivalents of zinc and 0.60 mgrm. equivalents of cadmium.

In Experiment 18 a solution containing 8 mgrm. equivalents of nickel carbonate was boiled one hour with 8 mgrm. equivalents of calcium sulphate. No nickel dissolved.

Fractional Precipitations with Sodium Bicarbonate.

Quantity taken (mgrm. equivalents).		Quantity precipitated (mgrm. equivalents).	
Experiment 35. (Time, nine days) —			
CuSO ₄	8.0	Copper	6.08
ZnSO ₄	8.0	Zinc	5.84
NaHCO ₃	8.0		
Experiment 36. (Time, three days) —			
CdSO ₄	8.0	Cadmium	5.46
ZnSO ₄	8.0	Zinc	1.60
NaHCO ₃	8.0		
Experiment 37. (Time, twenty hours) —			
HgNO ₃	8.0	Mercury	7.5
Zn(NO ₃) ₂	8.0	Zinc	None
NaHCO ₃	8.0		
Experiment 38. (Time, three days) —			
Pb(NO ₃) ₂	8.0	Lead	7.82
Cu(NO ₃) ₂	8.0	Copper	0.16
NaHCO ₃	8.0		
Experiment 44. (Time, twenty-four hours) —			
ZnSO ₄	8.1	Zinc	0.70
FeSO ₄	8.0	Iron	4.36
NaHCO ₃	8.0		
Experiment 45. (Time, eight days).			
ZnSO ₄	8.1	Zinc	2.14
NiSO ₄	8.0	Nickel	0.82
NaHCO ₃	9.0		
Experiment 46. (Time, eight days).			
ZnSO ₄	8.0	Zinc	1.06
AgNO ₃	8.0	Silver	2.90
NaHCO ₃	8.0		
Experiment 47. (Time, eleven days).			
AgNO ₃	8.0	Silver	3.70
MnSO ₄	8.0	Manganese	4.32
NaHCO ₃	8.0		
Experiment 48. (Time, twenty hours).			
ZnSO ₄	40.0	Zinc	12.1
FeSO ₄	40.0	Iron	21.2
NaHCO ₃	40.0		
Experiment 51. (Time, one day).			
FeSO ₄	32.0	Iron	9.16
MnSO ₄	32.0	Manganese	21.92
NaHCO ₃	22.0		
Experiment 52. (Time, five days).			
CuSO ₄	8.0	Copper	5.64
CdSO ₄	8.0	Cadmium	0.40
NaHCO ₃	8.0		
Experiment 53. (Time, five days).			
HgNO ₃	8.0	Mercury ..	Nearly all
Pb(NO ₃) ₂	8.0	Lead	Trace
NaHCO ₃	8.0		
Experiment 54. (Time, four days).			
HgNO ₃	8.0	Mercury ..	Nearly all
Cd(NO ₃) ₂	8.0	Cadmium ..	Trace
NaHCO ₃	8.0		
Experiment 57. (Time, five days).			
CdSO ₄	8.0	Cadmium	7.60
MnSO ₄	8.0	Manganese	5.96
NaHCO ₃	8.0		
Experiment 72. (Time, eighteen hours).			
ZnSO ₄	16.0	Zinc	6.84
MnSO ₄	16.0	Manganese	10.24
NaHCO ₃	16.0		
Experiment 88. (Time, five days).			
NiSO ₄	16.0	Nickel	1.88
CaSO ₄	16.0	Calcium	0.20
NaHCO ₃	16.0		

Summary of Results of Fractional Precipitation with Sodium Bicarbonate at 15°–20° C., arranged in the Order of Solubility deduced from the Experiments.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.	Ratio of major to minor constituent.
53.. ..	Mercury	Lead	(a)
54.. ..	"	Cadmium	(a)
37.. ..	"	Zinc	(a)
38.. ..	Lead	Copper	49·0
52.. ..	Copper	Cadmium	14·0
50.. ..	"	Ferrous iron	1·6
35.. ..	"	Zinc	1·0
57.. ..	Cadmium	Manganese	1·3
49.. ..	"	Ferrous iron	6·4
36.. ..	"	Zinc	3·4
89.. ..	"	Silver	92·0
51.. ..	Manganese	Ferrous iron	2·5
72.. ..	"	Zinc	1·5
46.. ..	Silver	"	2·7
44, 48 ..	Ferrous iron	"	1·7
45.. ..	Zinc	Nickel	2·6
88.. ..	Nickel	Calcium	9·4
	Calcium		
	Magnesium		

(a) Chiefly mercury.

In Experiment 20 a solution containing 8·81 mgrm. equivalents of cadmium sulphate and 8·81 of nickel carbonate was boiled five hours in the presence of 8·81 mgrm. equivalents of sodium sulphate. A small amount of cadmium was precipitated.

In Experiment 66 the attempted fractionation of manganese sulphate and silver nitrate resulted in a reduction of the silver salt and oxidation of the manganese.

In Experiment 70 the precipitate formed from the sulphates of manganese and calcium turned brown in about a quarter of an hour, showing a slight oxidation of the manganese. Further results are given in the table (see next column).

The results at higher temperatures show only minor changes from the series at ordinary temperatures. Zinc appears above cadmium, probably owing to the formation of oxide. Nickel appears above iron, but as there is some doubt about their relative positions in the series at ordinary temperatures, this change is not to be emphasised. This shows that the experiments at ordinary temperatures yield conclusions of fundamental significance.

In Experiment 86 the ferrous iron was partly oxidised, presumably at the expense of cupric sulphate. Of the iron in the filtrate 24 per cent was in the ferric condition. The experiments with ferrous salts were all made in a special precipitating flask in an atmosphere of hydrogen, so that oxidation by air was sufficiently avoided.

Summary of Results of Experiments with Carbonates.

1. Calcite introduced into a dilute solution of zinc sulphate precipitates the zinc slowly, requiring two or three weeks to precipitate most of the zinc.

2. Freshly precipitated calcium carbonate acts more rapidly in precipitating metallic salts than any other form, and aragonite and calcite follow in the order named.

3. The precipitating action of calcite on manganese, nickel, and silver salts is less marked than on zinc, cadmium, copper, lead, and mercury salts.

4. When a mixture containing two equivalents of two metallic salts, one equivalent of each, is precipitated by one equivalent of a soluble carbonate, a fractionation occurs, and the extent of this fractionation has been determined approximately for a large number of substances.

5. The series obtained, beginning with the metals precipitated to the greatest extent, with sodium carbonate at ordinary temperature is mercury, lead, copper, cadmium, zinc, ferrous iron, nickel, manganese, silver, calcium, magnesium.

Fractional Precipitations with Sodium Carbonate at 60–80° C.

Quantity taken (mgrm. equivalents).		Quantity precipitated (mgrm. equivalents).		
Experiment 78. (One hour at 60° C.).				
Hg(NO ₃) ₂	.. 16·0	Mercury		8·88
Pb(NO ₃) ₂	.. 16·0	Lead		5·2
Na ₂ CO ₃	.. 16·0			
Experiment 79. (One hour at 80° C.).				
Pb(NO ₃) ₂	.. 16·0	Lead		10·24
Cu(NO ₃) ₂	.. 16·0	Copper		6·68
Na ₂ CO ₃	.. 16·0			
Experiment 80. (One hour at 70° C.).				
Ag(NO ₃) ₂	.. 12·0	Silver..		11·00
MgSO ₄	.. 12·0	Magnesium		0·40
Na ₂ CO ₃	.. 12·0			
Experiment 82. (One hour at 70° C.).				
ZnSO ₄	.. 16·0	Zinc		13·80
FeSO ₄	.. 16·0	Iron		4·72
Na ₂ CO ₃	.. 16·0			
Experiment 83. (One hour at 70° C.).				
CdSO ₄	.. 16·0	Cadmium		14·32
FeSO ₄	.. 16·0	Iron		2·04
Na ₂ CO ₃	.. 16·0			
Experiment 84. (One hour at 70° C.).				
FeSO ₄	.. 16·0	Iron		0·68
NiSO ₄	.. 16·0	Nickel		10·0
Na ₂ CO ₃	.. 18·0			
Experiment 85. (One hour at 70° C.).				
CaSO ₄	.. 12·0	Calcium	Undetermined	
FeSO ₄	.. 12·0	Iron		8·44
Na ₂ CO ₃	.. 12·0			
Experiment 86. (One hour at 70° C.).				
CuSO ₄	.. 16·0	Copper		9·08
FeSO ₄	.. 16·0	Iron		6·72
Na ₂ CO ₃	.. 16·0			

These results are collected in the following table:—

Summary of Results of Fractional Precipitation with Sodium Carbonate at 60–80° C., arranged in the Order of Solubility Deduced from the Experiments.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.	Ratio of major to minor constituent.
78	Mercury	Lead	1·7
76	"	Copper	4·5
59, 62, 79	Lead	"	1·5
15	Copper	Cadmium	3·6
86	"	Ferrous	1·4
17	"	Silver	2·1
77	Zinc	Cadmium	1·1
82	"	Iron	2·9
67	Cadmium	Nickel	2·7
83	"	Iron	7·0
84	Nickel	"	15·0
73	"	Calcium	10·0
65	"	Silver	17·0
94	"	Manganese	1·0
85	Iron	Calcium	—
95	Manganese	"	Chiefly manganese
75	Calcium	Silver	1·5
80	Silver	Magnesium	27·0
	Magnesium		—

6. The series obtained with sodium bicarbonate at ordinary temperature is mercury, lead, copper, cadmium, manganese, silver, ferrous iron, zinc, calcium, magnesium.

7. The series obtained in warm solutions with sodium carbonate is mercury, lead, copper, zinc, cadmium, nickel, iron, calcium, silver, magnesium.

8. Silver salts are partly reduced by ferrous and manganoous salts; possibly also by nickelous salts, this effect becoming more marked as the alkalinity increases.

9. In the presence of bicarbonates zinc shows relatively greater solubility than cadmium, and nickel is likewise relatively more soluble than when precipitated with normal carbonate.

10. With rising temperature the precipitates from cadmium, iron, and silver salts appear to increase in solubility relatively faster than the others.

11. The presence of cupric sulphate greatly intensifies the tendency of ferrous salts to oxidise.

(To be continued).

ATOMIC WEIGHT OF CADMIUM.

By G. A. HULETT and E. L. QUINN.

IN an article on the atomic weight of cadmium, Baxter and Hartman (*Journ. Am. Chem. Soc.*, xxxvii., 113) obtained the value 112.114, and call attention to the disagreement between this result and that obtained by Perdue and Hulett (*Journ. Phys. Chem.*, xv., 1579), Laird and Hulett (*Trans. Am. Electrochem. Soc.*, xxii., 385), and Quinn and Hulett (*Journ. Phys. Chem.*, xvii., 780), where the value 112.3 was obtained by three independent methods.

Baxter and Hartman have pointed out some possible sources of error in our work, which we think should receive some attention. In the last article we analysed cadmium chloride by depositing the cadmium electrolytically in a mercury cathode. This was done in order to avoid the inclusions which are always present in electrolytic deposits and very pronounced in the case of cadmium (we have found as much as 0.085 per cent), but when the metal was dissolved in a mercury cathode there were no inclusions.

Baxter and Hartman have also analysed cadmium chloride by depositing the cadmium electrolytically in a mercury cathode, which was in a glass cell with a sealed-in platinum anode. These workers were unable to obtain all of the cadmium in a weighable form in their cell, and so made a correction for the cadmium in the electrolyte and wash-waters. Therefore they suspected that we overlooked cadmium in our electrolyte and wash-water. We concentrated our electrolyte and wash-water to a small volume, but were unable to find cadmium, but Baxter and Hartman make the objection that we must have had a strong acid solution in our test. This, however, was not the case, as we evaporated the electrolyte and wash-waters in a platinum dish and heated until the fumes of sulphuric acid ceased; the residue was then taken up with a very little water and tested in a volume of 1 cc. with hydrogen sulphide. Comparisons were made with known amounts of cadmium in the same volume. There may, however, have been a trace of acid in our tests, as we did not endeavour to expel the last trace of acid. So some special tests have been made by one of us (Quinn) in regard to this point. A volume of liquid equal to the electrolyte and wash-water and containing 1½ cc. of strong sulphuric acid was evaporated with known amounts of cadmium sulphate and the acid expelled just as in our previous work. The following amounts were taken:—1, 0.0002; 2, 0.0001; 3, 0.00005; 4, 0.00001 gram. of cadmium.

The first three tests showed cadmium at once and smaller amounts in time. In addition to these some tests were made with known amounts of acid present. On using an 18 per cent solution of sulphuric acid with known amounts of cadmium, as follows:—1, 0.00007; 2, 0.00006; 3, 0.00005; 4, 0.00004 cadmium in 1 cc. acid.

The first three were detected at once by the aid of hydrogen sulphide, and smaller amounts in time. We conclude, therefore, that we could not have overlooked a weighable amount of cadmium in our experiments. We weighed from 4 to 6.5 grms. of cadmium in analysing the

cadmium chloride, so there could not have been a loss greater than 1 part in 100 000 due to this cause.

Baxter and Hartman used a glass cell with a mercury cathode for decomposing their cadmium chloride, and always found cadmium in their electrolyte and wash-water; this corresponds with our earlier experience in using this kind of a cell, and is the reason for developing the cell we finally used. Our observation was that the difficulty was not inability to deposit all the cadmium in the mercury, but rather in the subsequent manipulations due to removing the layer of electrolyte which is always found between a mercury cathode and the glass part of a cell. In order to remove this layer of electrolyte and satisfactorily wash the amalgam it must be disturbed, and there is danger not only of oxidation but also of loss of finely divided amalgam. We found that this could be avoided by using a platinum cup amalgamated internally, so that the mercury cathode wet the cup, and it was therefore impossible for either electrolyte or water to get underneath the mercury. It was only necessary to wash the upper surface of the amalgam, which was not disturbed during the process. The amalgam and cup were strongly cathode during the process of replacing the electrolyte with water. The final wash-water was removed with a pipette, so that only a drop or two remained on the surface. Then the cup and amalgam were placed in a vacuum desiccator over a dehydrating agent, where the last traces of water rapidly disappeared, and there was no layer of water between the amalgam and cup to cause spurting. We took precaution to avoid any loss of mercury by evaporation, and convinced ourselves that the method was reliable by means of blank tests as follows:—We started with weighed pieces of our purest cadmium, dissolved these in hydrochloric acid, changed them to the sulphate, electrolysed in our cell, and weighed the cadmium in the mercury cathode, following every detail of the manipulation used in analysing the cadmium chloride. Five such tests were carried out. Two showed a gain and three a loss (the probable error of a single determination was ± 0.00004 grm.), so that our method of determining cadmium in cadmium chloride gave us results which we think can be relied upon to two or three parts in 100,000, and we conclude that the percentage of cadmium in the cadmium chloride we had was 61.217, with a probable error of not over 2 in the last decimal place. We question whether any method of analysis has been tested as rigidly as we have tested the method we used.

In our preliminary work we were unable to fuse cadmium chloride in a platinum tube in an atmosphere of hydrochloric acid gas without a measurable loss of platinum, but we found that with proper precautions this operation could be carried out in a quartz tube. Baxter and Hartman called attention to this part of our work, and concluded from a loss in one of our experiments of 2.9 mgrms. of platinum that we probably had air (oxygen) in our hydrochloric acid gas. We were using a Smith crucible with a much larger surface than an ordinary platinum boat, but aside from this the statements of Baxter and Hartman are quite misleading. They took the value 2.9 from a table recording five experiments. The losses were from 2.9 to 0.6 mgrm. of platinum. The loss with new platinum was large but decreased with use. This is ten times as large as the figures given in Baxter and Hartman's paper. In our method of preparing the hydrochloric acid we took precaution to exclude air, all of the joints of the apparatus were glass or glass sealed, and that it was gas-tight when evacuated was proven in each case. In fusing the cadmium chloride in a quartz tube we found no measurable loss in the weight of the tube.

In the work of Laird and Hulett (*Trans. Am. Electrochem. Soc.*, xxii., 385) a cadmium coulometer was developed which used a mercury cathode in an amalgamated platinum cup. There could be no inclusions in the cadmium deposited in mercury, while the washing and handling of the amalgam had the advantages of avoiding the presence of the electrolyte between the mercury

cathode and the cup. This coulometer was used in series with a silver coulometer, and the cadmium and silver deposited by the same current showed a value of 112.31 as the atomic weight of cadmium if we take the accepted value for silver. Baxter and Hartman remark that it is not easy to obtain a coulometer silver deposit in which the proportion of inclusions is known. We must take decided exception to this statement, as this work was done in conjunction with an extended investigation of the inclusions in electrolytic silver. We developed a direct method for determining these inclusions, and in the silver coulometer as used by us at that time the inclusions were 4.6 parts in 100,000, with a probable variation of about 0.5 part. Furthermore we made allowance for the inclusions in our electrolytic silver, as stated in the article referred to by Baxter and Hartman. This question of inclusions in electrolytic silver is one which we will take up in detail later, although it is too small to be of significance as far as the atomic weight of cadmium is concerned.

The first work done by us (Perdue and Hulett, *Journ. Phys. Chem.*, xv., 1579) after we had developed our method of determining cadmium deposited in mercury was an analysis of cadmium sulphate crystals. Cadmium sulphate crystallises with $8/3$ molecules of water and forms most remarkably perfect and clear crystals. The salt is not isomorphous with other substances and so offers an exceptional method of purifying the substance. The crystals are water-clear and do not show inclusions under highest magnification. They are very stable crystals, neither seeming to effloresce nor deliquesce in ordinary dry air. We observed the weight of a large crystal (5 grms.) for a period of several weeks and found no measurable change in weight, although we could have detected 0.01 to 0.02 mgrm. The crystal remained in the balance case during this period. This seemed remarkable at first, but it is quite possible that a perfectly pure hydrated salt may not have a definite vapour pressure. This would follow from the phase rule; if we had only vapour and $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ there would be two phases and two components, so it would require the presence of another hydrate or the anhydrous salt for equilibrium. In other words, we would not necessarily be restricted to a particular pressure for a given temperature; in fact the salt appeared to us to behave much like a supercooled liquid. Various samples of this carefully crystallised salt were analysed by depositing the cadmium in the mercury cathode, as described above. The results were very concordant and gave the value 112.3. We did not place much reliance on this value, as the determination of atomic weight by using a hydrated salt is of course questionable. Prof. Richards (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 888) has pointed out that there are always inclusions of mother-liquor in crystals; also he suggested the possibility of the solubility of water in these crystals. Both of these things are of course possible, but as far as the inclusion of electrolyte is concerned it was impossible to detect its presence by the use of a microscope; furthermore it might be pointed out that cadmium sulphate is a very soluble salt and the percentage of water in the saturated solution is not much over twice that in the crystals, so that it would require inclusions amounting to 1 part in 500 to affect the atomic weight of cadmium by as much as the amount in question. It is of course possible that there is a certain solubility of water in these crystals, since we must assume that every substance is soluble in every other substance, and there may have been a distribution of water between the solution and the crystals which would tend to give too small a percentage to the cadmium in the crystals. But this argument will also work in the other direction, since we must admit that the solute is also soluble in the crystals, and this would tend to give too great a percentage of cadmium in the crystals. There is, however, no definite information on these points, and so we merely regard the analysis of the crystals as interesting. — *Journal of the American Chemical Society*, xxxvii., No. 9.

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

April 6, 1916.

CINEMATOGRAPH LECTURE ON "THE MAKING OF A BIG GUN."

Dr. W. ROSENHAIN, F.R.S., of the National Physical Laboratory, delivered a lecture, illustrated by cinematograph pictures, under the auspices of the Faraday Society, on "*The Making of a Big Gun.*" The lecture was held in the rooms of the Royal Society of Arts and was presided over by Sir ROBERT HADFIELD, F.R.S., President.

The lecturer began by contrasting the "big guns" of olden times with the gigantic weapons of to-day. The older guns were made of cast-iron, and guns of that material reached their highest development in the American Civil War. The conditions existing in modern guns were illustrated by sectional diagrams relating to guns of fairly recent date, in which pressures of 18 tons per square inch and muzzle velocities of 2500 feet per second occurred. To resist these conditions, the best possible steel was required, and even that only served for a comparatively short time. The work of modern guns was illustrated by some photographs of gigantic projectiles which had been recovered intact after penetrating great thicknesses of modern armour. The effect of use on the inside of a gun was illustrated by photographs showing the "erosion" and the cracking which occur as the result of the high temperature of the explosion gases.

The lecturer then proceeded to describe the modern process of gun-making by the aid of a series of cinematograph pictures of the most interesting and striking stages of the process. These films had been prepared and lent to him by the courtesy of Messrs. Vickers, Ltd., at whose Sheffield works they had been taken. The series began with the blast-furnaces in which the iron ore is reduced by the aid of coke and limestone; next came the open-hearth steel furnace and the processes of filling were shown, and particular attention was drawn to a picture which clearly showed the "boiling" of the molten steel within the furnace. Throughout the various stages of the process, including the refining of the iron to transform it into steel, its various stages of forging, hardening, and tempering, the lecturer gave in popular terms the scientific reason for each step, illustrating his remarks by a series of photomicrographs showing the minute structure of the steel at each stage, and showing how each step served to bring the steel nearer to the ideal condition of perfect homogeneity. The lecturer naturally avoided reference to those confidential matters which relate to the most recent products of the steel-maker's art as directed to the production of guns, but as an indication of the direction in which modern practice tended, he showed the extremely minute micro-structure which can be produced by proper treatment in modern special or "alloy steels." The extreme importance of accurate scientific control, both of compositions, temperatures, and rates of cooling, throughout the process, was strongly emphasised and illustrated.

By means of the series of cinematograph films the gun was followed through its various stages, from the freshly cast ingot weighing 80 tons, through the processes of "cropping" and "trepanning," as the first piercing of the ingot to form a rough tube is called, on through the forging press until it attains its requisite length—in some cases over 70 feet. Then follow the machining operations, and then what is, perhaps, the most delicate part of the process—hardening and tempering, in which the roughly machined tube is heated to a uniform and carefully regulated temperature in a tall chimney-like vertical furnace, from which it is lifted at the proper moment to be plunged into an oil-bath contained in a deep cylindrical well. The process of rifling and the finishing of the outside, after the application of the wire-winding, were also

shown. Finally, as a relief to the more severely technical portions of the lecture, some films were shown illustrating the testing and firing of big guns.

Sir ROBERT HADFIELD, in proposing a vote of thanks to the lecturer, supplemented what he had said by some further interesting information with regard to the achievements of modern artillery. He spoke, for example, of 16-in. American guns firing a shell of 2400 lbs. weight a distance of 21 miles, and of a 12 in. armour plate fired at from a distance of $1\frac{1}{2}$ miles being cracked but not perforated. The wire-wound gun described by the lecturer was found to be the finest in the world, and it had the advantage of being cheaper than enemy patterns. It was not usually realised that the life of a large gun, based on the time of actual fire, was not more than three seconds.

A curious fact was that the soft-nosed cap used on modern shell expanded so rapidly on striking an object as to allow the complete shell to pass through it. In referring to the great importance of metallurgy in gun-making engineering, Sir Robert Hadfield told of a 15-in. shell which can pass through 15-in. armour plate in no more than $\frac{1}{1000}$ of a second, and of a 6-in. shell fitted with a modern cap which he had seen fired three times before the shell was broken.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 5, 1916.

Mr. GEORGE EMBREY, President, in the Chair.

Mr. Frank Theodore Alpe was elected a member of the Society.

A certificate was read for the second time in favour of Mr. Maurice S. Salamon.

The following papers were read:—

"On the Alkalimetric Estimation of certain Bivalent Metals in the form of Tertiary Phosphates, with Especial Reference to the Volumetric Determination of Cobalt and Nickel." By W. R. SCHOELLER, Ph.D., and A. R. POWELL.

Stolba's alkalimetric method for the estimation of phosphoric acid in magnesium ammonium phosphate is also used for the determination of magnesium, and has been extended to that of zinc in zinc ammonium phosphate. The authors have demonstrated the applicability of the process to cadmium, manganese, and cobalt. On dissolving cobalt ammonium phosphate in a measured volume of N/5 acid and titrating back the excess of the latter, the intense colour of the solution rendered most indicators useless. Results obtained with cochineal were always 0.5–2 mgrms. high, due to the action of cobalt on the indicator. By suspending cobalt ammonium phosphate in water and adding N/5 acid until the precipitate just disappeared, satisfactory results were obtained. It is shown that the nickel in the filtrate from cobalt ammonium phosphate can be titrated by cyanide without further manipulations; hence the phosphate process for separating nickel and cobalt allows a separate volumetric estimation to be made of the two metals.

"Note on a Specimen of Ancient Russian Oak." By P. A. ELLIS RICHARDS, F.I.C.

The author gives the results of his examination of specimens of oak that have been buried for many centuries in the sandy bed of the river Moksha in Russia. The chemical analysis shows that by the prolonged solvent action of water in the presence of a soil rich in iron the sodium and potassium salts originally present have almost entirely disappeared, whilst the percentages of iron and calcium compounds have greatly increased. The oak itself still retains its woody character, although the colour has changed to a dark grey or black.

"Estimation of Potassium in presence of other Substances." By A. H. BENNETT.

The author describes a method based on a combination of the cobaltinitrite and perchlorate processes which can be successfully used for the estimation of potassium in the presence of even considerable quantities of other substances, ammonium salts being the only bodies of common occurrence capable of interfering with the results. The method is particularly applicable in the case of wine lees, argols, tartars, and in the liquors of tartaric acid works, where potassium occurs with free tartaric acid, sulphuric and phosphoric acids, iron, alumina, and organic matter.

Precautions to be observed when phosphates of iron and aluminium are constituents of the mixtures analysed are given, together with results obtained by the use of the process under varying conditions.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

Fourteenth General Meeting, April 18, 1916.

Prof. J. CADMAN, C.M.G., M.Inst.C.E., President.

PRESIDENTIAL ADDRESS.

In opening the third session, and the first meeting at which it is my privilege to preside, permit me to thank you for the great honour you have conferred upon me in electing me to the Presidential Chair, and to express my fervent desire to fulfil the task you have set me to the credit and best interest of the Institution. The office is rendered the more difficult in that I have to take the reins from the so eminent and distinguished a technologist—Sir Boverton Redwood—but I am relieved to know that my shortcomings may be obscured by the kindly assistance of the council and officers with whom it will be my good fortune to serve.

I would ask you to consider for a few moments a matter which I venture to think is of considerable importance at the present moment, and as the time at my disposal is so brief, I am compelled to curtail my remarks within very limited dimensions.

The greatest assets of a country are its productive industries, and as these assets dwindle, as they inevitably must, the importance of oversea dominions must just as surely increase. But in our easy-going Empire the policy of drift has too long affected every department in life and industry, so that now we find that our oversea resources, which are great, have not been developed sufficiently to be our standby in time of need.

We have now reached a stage in the awakening of Britain at which we hear on all sides the reiterated determination that this policy of drift has got to cease forthwith and for ever. At this critical period it is not unnatural that the Institution should take stock of its responsibilities, responsibilities which we owe to the profession and to the Empire, and to this point I am going to confine my remarks.

Our individual responsibilities as members of the profession can be summarily dismissed, by stating that never before has it become so essential that efficiency and activity should be put into our individual labours.

Our responsibilities to the country opens up a very wide subject. From many quarters of the Empire evidence of petroleum is almost daily being recorded, and with the possibility of large reserves within the Empire a common policy of development and conservation is indicated.

To outline a policy here would perhaps be out of place, for serious consideration and discussion is necessary to assure a system which is applicable to every case. That it is possible, however, to formulate a scheme on general principles by which the most efficient results can be obtained from the capital expended is obvious. First of all, of course, a thorough geological examination of both proved and unproved territory is needed, and it would

seem desirable for Imperial purposes that all geological maps and reports, whether prepared by private enterprise or not, should be recorded. In this direction it is worthy of consideration whether State measures are not desirable to secure the co-ordination and interpretation of geological data for all the Empire's oilfields. In the second stage, that of investigation, in which test drilling is the determining factor, waste of capital and energy may be avoided by bringing to light both failures and successes. Whilst in the third period,—development, production, and refining,—the waste of petroleum and natural gas could be handled to advantage. That some definite policy is desirable may be detected by noting the amount of crude oil and natural gas that is daily running to waste on every oilfield.

To secure a uniform policy it would seem the duty of the various authorities within the Empire to confer with a view to common action, bearing in mind the requirements of the Empire as a whole, and in this direction the Institution might render valuable assistance.

Arising from this is the stock-taking of the actual petroleum resources, whether from oil-sands or oil-shales, and an enquiry upon this subject could be profitably prosecuted. A Committee of the Institute has already been formed to consider the oil-shales of the country, and it might with advantage consider a scheme to cover the more comprehensive problem of the Empire's petroleum resources.

Again, enquiry may be instituted concerning processes and methods which might render workable oil resources at present of little commercial count. The subject has already been ventilated in the technical press, and too much attention cannot be bestowed upon this important problem.

In order to carry out such an Imperial programme—if I may use such an expression—it becomes necessary to ensure a sound training for those who are to undertake responsible positions in the field. We have been in the past dependants upon German, Austrian, and other foreign technologists in our oilfields, but the time has come when we must make up lee-way and provide the Empire with efficiently trained British subjects. In the past experienced men were only available in foreign oilfields, and it is only within the last few years that an organised branch of the profession of petroleum technology has been in existence.

A good deal has already been done by the Government to stimulate such a policy, although only directed to Crown Grants of mineral oil concessions, and it is of interest to note that in some cases the Government has insisted upon the work being in the hands of British technologists.

The educational problem is complex. It must not be considered that the educational process is complete and sufficient in the hands of the Universities unless in active co-operation with works and oilfields, where a large part of the training must be accomplished. There is a danger of it becoming assumed that a boy can be converted into a petroleum technologist simply by sliding through a University curriculum. The practical training is as necessary as the theoretical, and one without the other lacks the fundamental foundations which are absolutely necessary in the educational preparation which all technological workers of the future must submit to, if this great industry is to be handled with organised efficiency.

The supply of materials is also a necessary adjunct of the policy just outlined, and in this respect British manufacturers must become alive to their responsibilities, and be prepared to manufacture every conceivable form of equipment and machinery which the peculiar characteristics of this industry demands.

Transport has an important bearing upon the rate of development of the potential zones within the less populated areas of the Empire. This has largely to be cultivated if the Empire is to profit by the rapid and cheap dissemination of petroleum and its products throughout the more thickly-populated and industrial centres. Cheap

and rapid transport facilities are indispensable, and a serious problem lies before the country to provide British-owned steamers for this purpose. There is little doubt that at the present time foreign enterprise largely caters for this traffic, and so long as the traffic is carried on primarily in the interest of foreign marketing companies, the full measure of development of British resources must be subject to such influence.

The future adaptation of liquid fuel for marine propulsion instead of coal is a subject receiving serious attention, and the solution of the problem will in some measure depend upon the introduction of fuel stations along the trade routes, similar to the present coaling stations, and there is already evidence of the formation of such stations.

The necessity for the harnessing of the petroleum resources of the Empire, so as to ensure the most efficient production and use of the product is a matter of great Imperial importance, and in this connection we cannot shrink from the fact that a grave responsibility rests upon us individually and collectively as members of the Institute of Petroleum Technology.

The PRESIDENT moved the following resolution:—

Ladies and Gentlemen,—It is my first and pleasing duty, as your representative, to move a resolution of thanks to our late President for the magnificent work which he has done for the science of Petroleum Technology, and for the untiring energy and ability which he has displayed in promoting this Institution, in nourishing it through that delicate period of incubation, and in bringing it with budding and promising youth to its present fully-fledged and healthy condition.

It would be presumption on my part—a 'prentice hand in comparison with the subject of my remarks—to attempt to give you an account of what Sir Boverton Redwood has done in a sphere which he has so long made his own. His association with petroleum dates back, I believe, to 1869, when, whilst working with his father, Prof. Redwood, he was appointed to undertake the secretarial duties of the Petroleum Association. It was here that he realised that the scientific treatment of the subject was necessary; it was here that he sowed those seeds which have done so much for the scientific development of an industry which embraces almost every corner of the civilised world.

I suppose there are few oilfields in the world which have not been visited by him, or have in some measure come under his careful guidance, and there are many that owe their successful development to his investigation.

His researches in all matters dealing with petroleum are historic, and he continues to make history, which every aspirant to become a petroleum technologist must needs study. His influence is felt in every corner of the globe from which petroleum is obtained and used. His work stands as a monument which will live for all time.

No professional technologist has rendered greater service to the State, and in his capacity of technical advisor to the Admiralty, Home Office, Colonial Office, India Office, Corporation of London, Thames Conservancy, Port of London Authority, and other public departments, his wide experience has always been at the disposal of his country.

From time to time as a member of some Royal Commission, as a president of some scientific society, his energy has been devoted to the furtherance of science, and in this capacity immeasurable service has been also rendered.

It was, I believe, about 1901 or 1902 that he was called to counsel by the Admiralty, to give to the State the great benefit of his wide knowledge and experience of oil fuel.

The subject was at that time receiving special attention, and from such intimations as reach the general public of the equipment of our warships, we know that oil as a naval fuel has made steady progress. In 1912 a Royal Commission on oil fuel was appointed by the Admiralty to investigate the subject further. Admiral of the Fleet

Lord Fisher of Kilverstone was chairman of that Commission, and Sir Boverton Redwood was one of a band of distinguished men who were selected to serve as members of the Commission.

All of us who know Sir Boverton can well imagine how greatly honoured he felt at the confidence which the Government thus showed in his knowledge and judgment, and none of us who know him will need to be told with what energy he threw himself into that work, which was to him a labour of love and at the same time a duty of a very sacred character.

For many years he has given his service to the Admiralty in an honorary capacity, because of his sincere desire to serve his country by giving the best that was in him—how good that best is we all know.

Sir Boverton had profound faith in the merits of oil as a fuel, and we know that he has been a consistent advocate of its use for naval purposes. He had a firm faith that Mother Earth would not fail to produce the needful supplies.

I might here relate an incident as described by an eyewitness. During the sittings of the Royal Commission, Sir Boverton was unfortunately deprived for a short time of his usual active powers of getting about. His devotion to duty was such, however, that he insisted on attending the sittings on the Commission, although on one occasion this necessitated his being carried into the room. I am told that the sympathy of his colleagues and their appreciation of his devotion was markedly displayed on that occasion.

I am sure that Sir Boverton will regard it as one of the most pleasant and honourable incidents of his career that he was able, and had the opportunity, to render important service to the great Navy upon whose efficiency the maintenance of our national existence depends.

Those who have listened to his addresses upon the subject of liquid fuel could not help being impressed with his masterly grasp of the subject. His paper upon Liquid Fuel before the Seventh International Congress of Applied Chemistry in 1909 is worthy of special attention, for it rang a note which still vibrates in the ear of every student of this great problem.

It is not necessary for me to allude to his standard Text Book on Petroleum, which is so well known. I expect every person in this room has at some time or other extracted information from his Redwood, and has silently had cause to bless its author.

Upon the subject of Invention, our late President has been no mean investigator. The Redwood viscometer and other testing appliances are in daily use, and have established standard procedure based upon scientific principles, which alone will perpetuate the name of this master-hand in future generations.

As an Educationist his valuable assistance in the introduction of courses in Petroleum Technology at the Imperial College of Science and Technology, and the University of Birmingham, have been greatly appreciated, and the fruits of this phase of his activity will, I venture to predict, be in time a boon to activity of Petroleum Technology in the country.

Besides the many works of imperial and international importance, there is one phase in this great character to which I must allude, for nearly every member and associate member of this Institution has experienced that unflinching kindness, helpfulness, and inspiration which he so ungrudgingly and unselfishly showers upon us. Sir Boverton's personal interest in, and benevolent advice to, all of us has been so constantly and so freely given, that we may be in danger of forgetting how much it has meant to the Institution.

In the midst of an intensely active career, which we hope will continue for many years to come, he has never been too busy to help the newcomer and to stimulate him to fresh efforts.

I need not remind you that we are losing a President whom none can hope to replace, but the blow to this In-

stitution is fortunately tempered by the fact that as a Vice-President his helping guidance will still be with us.

That such an Institution as this is possible, is due to his genius; that it has entered successfully upon a life of ever-increasing activity and usefulness, is due to his experienced guiding hand; that its aims are high and worthy, is a reflection of his personal character.

I fear it is too much to hope that the mantle which falls from Sir Boverton's shoulders may descend upon his successors in office, but he has raised a standard which we shall be proud to bear to the best of our ability; strong in the atmosphere of kindly co-operation which he has done so much to create; and trusting that inevitable shortcomings may be lightly criticised.

I now have the honour to ask you, Sir Boverton, to accept our warmest appreciation of the very valuable services you have rendered to the Institution during the two years in which you have held the office of President with such conspicuous and brilliant success, and I ask you, ladies and gentlemen, to show your approval with acclamation.

NOTICES OF BOOKS.

The Physical Properties of Colloidal Solutions. By E. F. BURTON, B.A. (Cantab), Ph.D. (Toronto). London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1916. Pp. vii. + 200. Price 6s. net.

THE phenomena of colloidal solutions are considered in this book with special reference to their bearing on the development of physics, and students of this science will find that it contains a highly interesting account of the subject. The book has perhaps a rather wider scope than the title would suggest, and the text is so admirably clear and graphic that no student could fail to be interested in it. The general properties of colloidal solutions and the theory of their formation are first discussed, while a short outline is given of their application in many branches of industry. One of the best features of the book is the excellent historical and descriptive treatment of the ultra-microscope and the detailed account of the study of the Brownian movement, in which is included a summary of the results of the determination of molecular constants by various methods. The work recently done on this subject constitutes one of the most wonderful chapters in the history of the development of modern science, and it has been well summarised here. The author has included in the text many interesting and well chosen quotations from the works of modern physicists and an excellent bibliography which adds greatly to its value.

The Proceedings and Transactions of the Nova Scotian Institute of Science, Halifax, Nova Scotia. Vol. XIII. Parts 3 and 4. Vol. XIV. Part I. Halifax: The Royal Print and Litho, Ltd.

ONE of these volumes of the Proceedings of the Nova Scotian Institute of Science (xiii., 3) contains an interesting account of the events which led to the foundation of the Institute, with short biographical sketches of its deceased presidents and other prominent members. The various papers which are included cover very different fields of research, and bear witness to the vitality of the Institute and to the growing interest of the Nova Scotian educated public in scientific matters. Although not much more than fifty years old the Institute has done good work, especially in collecting the results of the investigation of the natural history of the province. It has done much to assist the work of the Provincial Museum, and has established a good library, which is rapidly growing. The papers printed in these volumes of the Proceedings deal with physical, geological, zoological, and other subjects, and include for the first time one on psychology—"Coloured Thinking," by Dr. Fraser Harris—which aroused animated discussion.

CORRESPONDENCE.

FAT ANALYSIS.

To the Editor of the Chemical News.

SIR,—Permit me to call your attention to the fact that the article by Mr. F. H. Smith, entitled "Notes on Fat Analysis," which appears in the CHEMICAL NEWS of December 31, 1915 (cxii., 319), presents the method for the determination of saponification number, soluble and insoluble acids, in almost exactly the form given in the "Official and Provisional Methods of Analysis of the A.O.A.C.," as published in the Bureau of Chemistry Bulletin No. 107, revised, pp. 137—9.

There are a few minor variations, however, which appear to me to detract rather than improve on the A.O.A.C. method. For instance, if the directions given by Mr. Smith are followed exactly, using a 250 cc. Erlenmeyer flask, when the insoluble fatty acids are liberated one will have only about 150 cc. of solution, which is insufficient to bring the cake of acids into the neck of the flask, where it is most readily collected. Also, Mr. Smith recommends the titration of one-fifth of the entire solution of soluble acids, while the official method calls for the titration of the entire filtrate. In work with oils which contain small amounts of soluble acids the latter method is preferable, as the total number of cc. of N/10 HCl required is often very small.—I am, &c.,

H. S. BAILEY, Food Investigation Chemist.

Department of Agriculture,
Bureau of Chemistry, Washington, D.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xix-xx., No. 2, 1916.

Saponification of Benzoyl Cyanhydrines by Acetic Acid in presence of Metallic Salts.—J. Aloy and Ch. Rabaut.—The authors have already described a certain number of benzoyl cyanhydrines of aldehydes and ketones. The amides corresponding to these cyanhydrines are generally prepared by saponification with mineral acids, but in some cases the reaction occurs only with difficulty and may even not occur at all. It has been found that the action of zinc upon an acetic solution of benzoyl cyanhydrines does not give rise to amines but to the corresponding amides. The reaction occurs very easily and with a good yield with the cyanhydrines of the aldehydes (benzoic, paraoxybenzoic, anisic). It is possible to replace the zinc by the oxide or acetate without appreciably diminishing the yield. The ingredients—cyanhydrine acetic acid, zinc oxide—are heated together for one or two hours and then poured into water, when precipitation usually occurs at once. The amide is then purified by crystallisation in alcohol. The zinc oxide can be replaced by oxides of mercury, silver, nickel, cobalt, and copper, but not by those of lead, cadmium, aluminium, iron, chromium, thorium, or the alkalis or alkaline earths. Manganese oxide has a favourable but feeble action. The oxide and acetate can sometimes be replaced by other salts; e.g., the sulphates of zinc or copper; cobalt chloride, however, has no action.

Action of Phenyl Isocyanate: Phenyl Homologues of Eserine and Geneserine.—Max Polonovski.—The author has studied the action of phenyl isocyanate on eseroline and geneseroline, and has collected in a table the results of his experiments on all the methyl and phenyl-carbaminic compounds of the eserine and geneserine groups. It appears from this table that in a general way

phenyl and methyl isocyanates behave similarly, giving with eseroline monomolecular compounds of the urea or urethane type and bimolecular ureo-urethane compounds. However, there are some differences in the two isocyanates; thus, C_6H_5CNO does not give a compound of the ureic type, a phenyl homologue of isoeserine. On the other hand, it gives the bimolecular ureomethanic type more readily than CH_3CNO . Geneseroline gives only a single urethanic compound, which seems to confirm the absence of the imide group in this substance. Both eserine and eserethol give with C_6H_5CNO mono and bicarbanilide compounds while they do not react with CH_3CNO . The fixation of $RCNO$ on the hydroxyl by etherifying the OH group of acid function considerably increases the basicity of the product. The bimolecular ureo-urethane compounds are quite neutral and are mostly insoluble in acids. The urethanes have a lower melting-point and a feeble levorotatory power than their ureic isomers, and their solubility in ether and benzene is much greater. The addition products formed by condensation in a neutral medium are decomposed practically instantaneously by alkalis in the cold, while the urethanes are decomposed fairly rapidly on heating and the ureas and ureo-urethanes more slowly.

Determination of Zinc by Electrolysis.—F. Chancel.—To get a good deposit of zinc by electrolysis it is necessary to have a uniform current so that there is not an accumulation of zinc in certain places and the deposit becomes spongy. Also, the solution must possess a fairly constant acidity. The cathodes should consist of platinum covered with mercury. The electrolyte is prepared by dissolving zinc in sulphuric acid, neutralising with ammonia, then adding sulphuric acid and sodium formate. By this method all the zinc is deposited in a convenient form and can easily be washed.

MISCELLANEOUS.

Special Reports on the Mineral Resources of Great Britain.—The Board of Agriculture and Fisheries desire to give notice of the publication of Volume IV. of the above named Special Reports which have been prepared by the Director of the Geological Survey in response to numerous inquiries that have arisen through the conditions brought about by the war. Volumes I., II., and III. are already published, and this, the fourth of the series, deals with the properties, sources, and uses of fluorspar, and gives details of all workings in Britain. Price, 9d. Copies may be obtained through any bookseller from Messrs. T. Fisher Unwin, Ltd., 1, Adelphi Terrace, London, W.C., or from the Director General, Ordnance Survey Office, Southampton.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Liquid Smoke.—In reply to Mr. Watson's enquiry (CHEMICAL NEWS, cxlii., 24), several preparations under the names of Ess. of Smoke, Cambrian Ess., Westphalian Ess., &c., are used in preserving ham and meat. For composition see—"Pharmaceutical Formulas," 1888, p. 487; "Cooley's Cyclopaedia," 6th ed., p. 660; Haldane's "Workshop Receipts," 1890, p. 288. Probable makers would be Boake, Roberts, and Co., Stratford, London, E., or it is likely to be stocked by dealers in butchers' requisites.—T. S., Sydney, N.S.W.

MEETINGS FOR THE WEEK.

MONDAY, May 1st.—Society of Chemical Industry, 8. "Evaporation of Naphthalene in Dry and in Moist Coal Gas," by J. S. G. Thomas. "Historical Summary of our Knowledge of Sulphur in Coal Gas," F. Clowes.

WEDNESDAY, 3rd.—Society of Public Analysts, 8. "Salvarsan and Neo-Salvarsan, Excretion and Secretion of," by W. H. Wilcox and J. Webster. "Microscopical Methods," by H. G. Greenish.

THE CHEMICAL NEWS

VOL. CXIII., No. 2945.

THE USE OF OZONE FOR CHEMICAL RESEARCH AND INDUSTRIES.

(Concluded from p. 116).

Research Apparatus.

THE standardisation of research apparatus for the laboratory is a great convenience to the chemist who wishes to make investigations with ozonised air under his own superintendence and control. Such outfits cannot, however, be built up from the apparatus found amongst an ordinary laboratory equipment, as they include parts which cannot be used for any other purpose. Standardised outfits which will cover the whole range of possible laboratory or research work are, however, available. The most important item of these outfits is the Ozone Generator with the high tension transformer for furnishing the necessary high voltage, and in addition, where a continuous current only is available, a rotary converter.

A small switchboard is always advisable, mounted with the necessary controlling and regulating apparatus, and an ammeter or a wattmeter is useful although not absolutely necessary for small experiments. The outfits should include the necessary aspirator or pump for drawing or pushing the ozonised air through the material to be experimented with, treatment and air drying vessels, &c., but in some cases these bottles, vessels, &c., and the connection tubes and corks may be omitted if the user is already in possession of such accessories.

Ozone generators are standardised in several sizes. Fig. 2 shows a small generator suitable for ordinary experiments of a qualitative or quantitative nature. It is mounted on a rigid metal frame and enclosed in a bell-glass, which is mounted on a glass-lined base provided with a stopcock. The top of the bell-glass is fitted with an outlet tube for the ozonised air and the necessary high-tension terminals. This generator can be used with air or oxygen, and concentrations from air up to 6 grms. of Ozone per cbm. may easily be obtained with suitable conditions. All the technical applications of Ozone, such as sterilising water, bleaching, and deodorising of various substances, preparation of chemicals, &c., can be performed with this apparatus on a small or trial scale. The yield of Ozone at a concentration sufficient to bleach oils, fats, &c., is about 1 gram. per hour, while the energy used in the generator will not exceed 25 watts for alternating current supply.

A larger type of Ozone generator is illustrated by Fig. 3, which is a reduced size of the generator referred to for industrial processes. It is intended for experimental investigations on a more extended scale and under similar conditions to the actual commercial operation. The electrodes, which are of special design, are contained in a water-tight aluminium case, capable of working under pressure. The high tension connecting cables are arranged with plug fittings, so that they can be readily disconnected. The range of concentrations with this apparatus is very large, and the treatments can be carried out in an expeditious manner involving a minimum of labour. With an energy consumption in the generator of 100 watts, the yield of Ozone is about 4 grms. per hour at a concentration sufficient to bleach oils, &c. The capacity for bleaching in a day of ten hours may be as high as 50 lbs. of certain materials. At lower concentrations the yield will be greater, and *vice versa*.

A new type of Ozone generator has recently been designed which is particularly valuable for research work, as it enables concentrations to be obtained up to 8000 parts

per million, equal to 16 grms. of Ozone per cbm. of air. This concentration implies that 4 per cent of the oxygen of the air is ozonised, the highest figure which has yet been obtained by any apparatus. This new type can always be used in place of Fig. 3 in the outfits about to be described.

The diagrammatic illustration (Fig. 4) shows a small outfit consisting of air-drying bottles, ozoniser, treatment bottle, aspirator, transformer, and switchboard. The Ozone generator is of the small size with bell-glass. The aspirator is of 9 to 10 litres capacity, and the maximum rate of the outfit is about 10 litres in five minutes. The aspirator must therefore be refilled after each 10-litre run, so that the experiment in some cases cannot be worked continuously.

Where continuous working is required and only qualitative results desired a Bunsen tap pump may be substituted

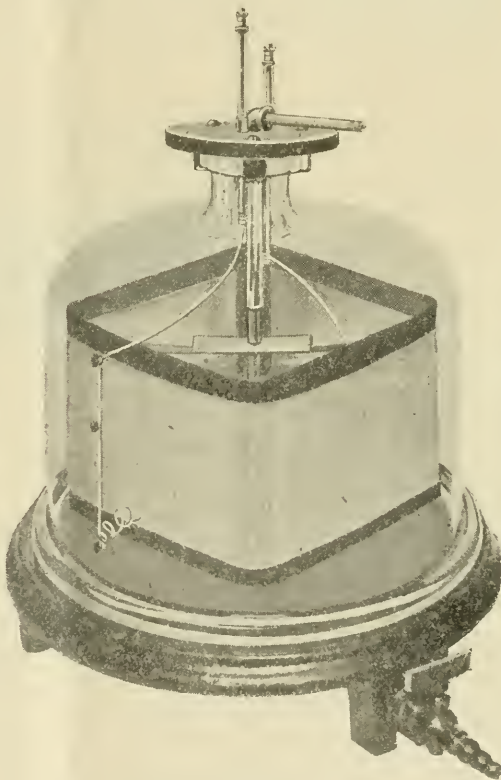


FIG. 2.

tuted for the aspirator, but where quantitative results and continuous running are required a small suction air-pump and electric motor can be substituted for the aspirator, by which the rate may be increased up to about 30 litres per minute. In this case, as the aspirator is not used, an air meter is employed, with a maximum reading of 40 litres per minute.

A larger outfit includes the aluminium Ozone generator, electrically driven air-pump and an air meter, and the apparatus as described for the previous outfit, but all slightly larger, and an absorption bottle is included for the absorption of any other gases, in order to leave the ozonised air absolutely pure. This outfit has a capacity of about 60 litres per minute.

A still larger outfit is recommended for work on a more extended scale. Its capacity—namely, 120 litres per minute—is double the size of the previous outfit, and it is in fact a miniature industrial installation adapted to the laboratory. The ozonised air, instead of being drawn

through the liquid to be treated, is forced under considerable pressure through small injectors, which have the effect of bringing the Ozone into intimate contact with the whole of the substance to be treated, so that a better result is obtained in a shorter time, and therefore with a smaller expenditure of Ozone. Moreover, certain treatments can be performed which by any other means would be impossible.

The set comprises an air cleaning and drying apparatus, an electrically driven air-pump, air meter, air cooling apparatus, Ozone generator, spraying injectors, treatment vessel, transformer, and switchboard. The air-cooling apparatus is not essential except for very exceptional circumstances or in hot climates, and could be dispensed with altogether if the new type of Ozone generator is used. The air cleaner and drier is of advantage, because it enables a considerable increase of yield to be obtained, whilst the possibility of the formation of the oxides of nitrogen at very high concentrations is eliminated.

In conclusion it may be pointed out that whilst the foregoing remarks give a fairly wide indication of the field in

THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES.*

By ROGER C. WELLS.

(Concluded from p. 199).

SILICATES.

Previous Work.

SINCE many of the natural silicates have been formed under the condition of equilibrium with a magma it is obvious that they will not be in equilibrium with aqueous solutions. In order to complete the study of fractional precipitation, however, it appeared desirable to see if there would be any selective action when solutions containing more than one metallic salt were precipitated by a soluble silicate. Jordis has already studied the precipitation of single metallic silicates from soluble salts with reference to

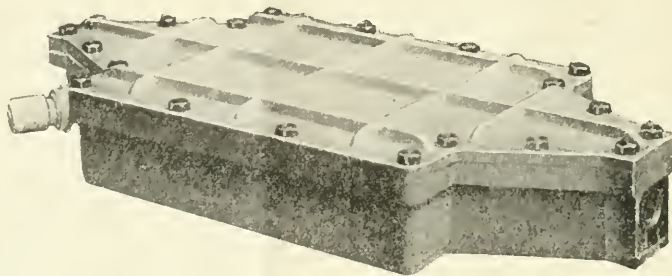


FIG. 3.

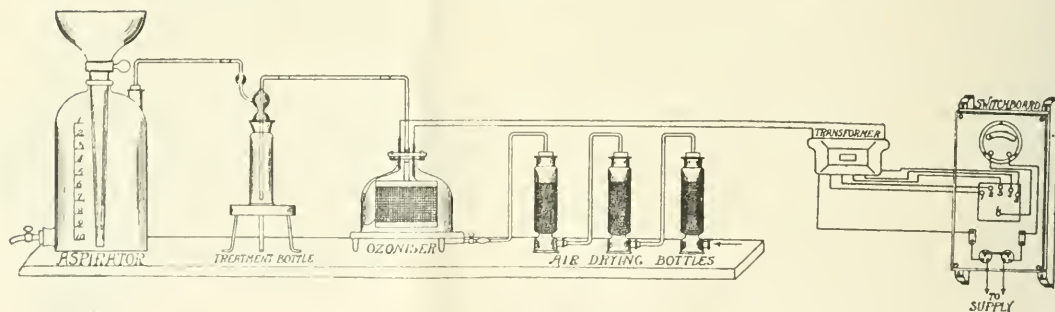


FIG. 4.

which Ozone has been proved to play an efficient part, and also of one method of applying the industrial treatment, there is still a very large unexplored tract for the chemist to investigate, particularly amongst the complicated benzene and other organic compounds and derivatives of coal-tar, &c. In this connection it may be hinted that Ozone in some cases acts something like a catalyst in the presence of another oxidiser, in promoting oxidation, which in its absence does not take place. By this is implied that with certain substances the theoretical quantity of Ozone required to perform the process of oxidation may appear to be so large as to preclude its employment on economic grounds, whereas actually the presence of a relatively small quantity of Ozone will induce oxidation by another oxidising reagent to the extent of as much as twenty times more than without Ozone.

We may add that we are indebted to Messrs. Ozonair, Limited, of 96, Victoria Street, London, S.W., for the illustrations and information regarding industrial plants and research apparatus.

their composition ("Zur Chemie der Silikate," *Zeit. Angew. Chem.*, 1906, xix., 1697; *Journ. Prakt. Chem.*, 1906, lxxvii., 226; 1910, lxxxi., 303). His experiments with ferric salts, however, are probably complicated by the phenomena of hydrolysis, but he suggests that the behaviour of colloids must be considered (E. Jourdis and P. Lincke, "Beiträge zur Kenntnis der Metall-silikate," *Journ. Prakt. Chem.*, 1910, lxxxi., 289).

Experiments with Silicates at Ordinary Temperature.

My own experiments have consisted of attempts at fractional precipitations of metallic salt solutions by amounts of soluble silicates insufficient for both the metallic constituents. Although it was expected that the sodium silicate, being hydrolysed, would behave like caustic soda, it seemed desirable to determine whether the silicic acid would participate in the reaction. After the results with the

* Bulletin 609, United States Geological Survey.

hydroxides, it was not surprising to find that in general one metal was precipitated to a greater extent than the other. Moreover, most of the silica was carried down with the precipitate. The results are shown in the following table, where the concentrations are expressed in millimoles per litre, 1 millimole being a thousandth of the molecular weight taken in grms. A diluted water-glass solution was used as the soluble silicate. The ratio of SiO_2 to Na_2O in it was 3.09 to 1.00. It was free from other metals except for a trace of iron and alumina. After precipitation the solution stood at about 30°C . for the periods noted in the table. The last column in the table shows the silica not precipitated by the metallic salts present. Sulphates were used except with lead and calcium salts, where nitrates were employed.

Results of the Fractional Precipitation of Silicates, arranged in the Order of the Solubility Deduced from the Experiments.

Experiment.	Time (days).	Quantities precipitated (millimoles).	SiO_2 not precipitated (millimoles).
114	97	4.8 copper, 0.2 lead, 11.2 SiO_2	4.0
115	91	6.7 copper, 0.7 zinc, 12.8 SiO_2	2.4
116	91	6.6 copper, no cadmium, 12.2 SiO_2	3.0
117	107	8.1 zinc, 5.6 manganese, 13.0 SiO_2	3.2
118	97	5.1 zinc, 0.1 silver, 11.9 SiO_2	3.3
119	31	5.1 zinc, 2.6 nickel, 10.5 SiO_2	4.7
120	102	5.9 manganese, 4.2 cadmium, 12.9 SiO_2	2.3
121	31	Very little cadmium and zinc, 12.5 SiO_2	2.7
122	95	5.13 nickel, no calcium, 12.9 SiO_2	2.3
123	97	4.8 magnesium, 0.2 calcium, 13.0 SiO_2	2.2
124 (a)	95	13.0 nickel, 0.8 calcium, 28.1 SiO_2	2.3
125 (a)	95	10.7 magnesium, 2.9 calcium, 27.6 SiO_2	2.8

(a) Double quantities taken.

Quantities taken in each experiment:—

- 9.10 millimoles M_2SO_4 per litre of the mixture.
- 9.10 millimoles M_2SO_4 per litre of the mixture.
- 4.95 millimoles Na_2O , 15.2 millimoles SiO_2 per litre of the mixture.

Summary of Results of Experiments with Silicates.

From the above results it appears that:—

1. The order of precipitability of the metals by soluble silicate solutions is roughly as follows, beginning with the most precipitable:—Copper, zinc, manganese, cadmium, lead, nickel, silver, magnesium, calcium.
2. The metals are precipitated almost as they would be by solutions of caustic soda, so that no marked specific effect appears to be due to the presence of the silicate.
3. Most of the silica is precipitated.
4. Some silica remains in solution, even with an excess of the metallic salt, and the quantity that remains appears to be independent of the nature of the metallic salt.

GENERAL VIEW OF THE RESULTS OF THE INVESTIGATION.

For comparison the several series obtained in the study of fractional precipitation in aqueous solution have been brought together in the table (see next column).

It would be possible to work out still other series by fractional precipitation. For example, the series of

Order of Solubility for each Class of Compounds Deduced from these Experiments on Fractional Precipitation.

Sulphides.	Carbonates.	Bicarbonates.	Hydroxides.	Silicates.
Palladium ..	—	—	Ferric	—
Mercury ..	Mercury	Mercury	Aluminium	—
Silver ..	Lead	Lead	—	—
Copper ..	Copper	Copper	Copper	Copper
Bismuth ..	—	—	—	—
Cadmium ..	Cadmium	Cadmium	—	—
Antimony ..	—	—	—	—
Tin ..	Zinc	—	Zinc	Zinc
Lead ..	—	—	Lead	Man-ganese
Zinc ..	—	—	—	Cadmium
Nickel ..	Iron	—	—	Lead
Cobalt ..	—	—	—	—
Ferrous ..	Nickel	—	Nickel	Nickel
Arsenic ..	—	—	—	—
Thallium ..	Man-ganese	Man-ganese	—	—
Manganese .	Silver	Silver	Silver	Silver
		Ferrous	Ferrous	
		Zinc	Man-ganese	
	Calcium	Calcium	Magnesium	Magnesium
	Magnesium	Magnesium	Calcium	

chlorides would be relatively short, whereas that of the phosphates would be longer, for most phosphates are insoluble. The compounds studied, however, cover the ordinary geologic transformations, and the studies show the general relations. Furthermore, in the tabulation of the results no attempt has been made to do more than arrange the several series in parallel columns. By a scheme that would exhibit cross relations all possible compounds might be arranged in a single series that would show the order of precipitation under like conditions. Such a series, however, would have little practical application for several reasons. A comparison of two compounds with no common radicle would really imply the possible existence of at least four compounds, a degree of complexity greater than that considered in the present study of fractional precipitation. Furthermore, the effects of mass action are always conjoined with the solubility requirements, a fact illustrated by the relations of certain silver haloids at Tonopah, Nev. (J. A. Burgess, "The Halogen Salts of Silver and Associated Minerals at Tonopah, Nev.," *Econ. Geol.*, 1911, vi., 13). In this locality silver chloride, cerargyrite, was deposited before the chlorobromide, embolite, and the iodide, iodyrite, which is more insoluble than the cerargyrite, probably because of the great excess of chlorides in the original solution. This series well illustrates the application of the mass law. Silver iodide is more insoluble in water than silver chloride, but if a solution of a silver salt meets a solution containing a great deal of chloride and very little iodide, after mixing (it being assumed for argument that precipitation does not occur instantaneously) the silver ion concentration will have a fixed value, the chloride ion concentration will be very large, and the iodide ion concentration very small. Hence the solubility product of silver chloride will be exceeded and that of silver iodide not be exceeded, although the solubility product of silver chloride is larger than that of silver iodide. Silver chloride may therefore be deposited before silver iodide, in apparent contradiction to the stated solubilities of the two compounds in water. On the other hand, the solubility of a compound in water is one of its most important properties, and it was to determine the order of these solubilities that these experiments on fractional precipitation were made.

THE SOLUTION OF THE CERIUM GROUP
OXIDES BY CERTAIN ACIDS.

By W. S. CHASE,

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As is well known, the oxides of the trivalent rare earth metals are moderately strong bases, resembling the alkaline earth oxides in that respect. With this fact in mind one would expect that the addition of a dilute mineral acid to a mixture of cerium group oxides would effect the quick solution of the more basic earths with but slight action on the least basic. If this did occur the result would be the complete separation of CeO_2 , which is the least basic of all the rare earth oxides and very resistant to acids. Such a separation, which indeed would constitute a rapid and easy method for the extraction of cerium, might be expected when it is considered that the other oxides present are for the most part among the more basic of the rare earth oxides (Levy, "The Rare Earths," p. 117).

Unfortunately the addition of dilute or even concentrated acid does not produce the expected result, and this must be due to the influence of the CeO_2 . This substance is practically insoluble even in hot concentrated acids, except sulphuric acid. It possesses the power of combining with the other rare earth oxides, and to this combination is undoubtedly due the failure of acids to react with the mixture of oxides in the manner that might be expected. Another result of this combination is that the CeO_2 when thus combined dissolves readily in acids in which it is otherwise insoluble provided its value in the mixture does not exceed 55 per cent. Therefore on treating the mixed oxides with acid the basic earths do not rapidly dissolve and the CeO_2 remain untouched, but instead the entire mixture goes into solution at a moderately rapid rate. This behaviour is rather remarkable in view of the fact that CeO_2 itself is practically insoluble, and that the other oxides by themselves will dissolve instantly in a small excess of very dilute acid.

The rate of solution of the mixed oxides can be very greatly increased by the addition of some substance that will reduce cerium to the cerous condition. Hydrogen peroxide answers this purpose admirably, for not only is the reaction very rapid and complete but there is the added advantage that no other salt is introduced into the solution (as is the case, for example, when KI or FeCl_2 , &c., are used).

Experimental.

The rare earth residue obtained after the extraction of thorium from monazite sand was the material used in this work. This residue consists essentially of the oxides of the cerium metals, though possibly small quantities of the yttrium elements may be present. No attempt was made to separate the latter, as they were not in sufficient quantity to be detrimental in any way. The principal constituent of the mixed oxides was of course CeO_2 , with a value of 52.70 per cent, the others in order of importance being Nd_2O_3 , La_2O_3 , Pr_4O_7 , and Sa_2O_3 .

The composition of the ordinary commercial residue is quite constant, the CeO_2 value, for instance, fluctuating between 50 and 60 per cent, and in most cases being around the mean of those values. The colour of the mixed oxides varies from reddish brown to chocolate, depending on the composition of the sample, ignition temperature, &c. (Levy, "The Rare Earths," p. 119). Their solubilities in sulphuric, hydrochloric, nitric, and acetic acid of different concentrations were studied, as was also the use of H_2O_2 as a reducing agent for CeO_2 .

The theoretical quantity of acid required to react with 1 grm. of sample was calculated on the basis of $\text{RO}_2 = 55$ per cent, $\text{R}_2\text{O}_3 = 45$ per cent (about the average composition of the residues handled in this laboratory), and the following figures were thus obtained:—

Acid.	Sulphuric.	Nitric.	Hydrochloric.	Acetic.
Approximate strength	96 p.c.	70 p.c.	38 p.c.	99.5 p.c.
Cc. per 1 grm. sample	0.58	1.33	1.7	1.2

Sulphuric Acid.—As is well known, with a large excess of acid and evaporation to strong fuming complete solution is obtained. The CeO_2 dissolves with but slight reduction, so that the solution is of a yellow or yellowish red colour, due to the ceric sulphate. However, this process is rather tedious, and as it is desirable that the fuming operation be avoided if possible, the action of H_2O_2 along with dilute H_2SO_4 was tried.

A few experiments sufficed to show that with a moderate excess of acid diluted as much as 1:10 or more, and a similar excess of H_2O_2 , solution is rapid and thorough. For example, 1 cc. each of acid and 30 per cent H_2O_2 and 10 cc. of water were added to 1 grm. of the oxides and the mixture heated for three minutes, by which time solution was complete. This experiment indicates that these oxides are dissolved by dilute $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ much more rapidly than by concentrated H_2SO_4 alone, and, further, the fuming nuisance is also avoided.

Nitric Acid.—The mixed earths dissolve fairly readily in this acid, which is most efficient when concentrated. However, when diluted, even as much as 1:2, it still acts fairly satisfactorily though somewhat slowly. When the acid alone is employed it is always necessary that a considerable excess be taken, but the quantity of the latter naturally decreases as the size of the sample increases. With the smaller samples, in order to avoid the use of a very great excess of acid the same should be diluted, which serves to increase the volume enough so that all the acid is not boiled off before complete solution can occur. These points are indicated by the following data:—

Sample used. Grms.	Nitric acid used			Total cc. of liquid at start.	Minutes required for solution (approximate).
	Parts acid.	Parts water.	Times theoretical.		
1	1	2	6	24	7
3	1	2	4	48	20
5	1	2	3	60	20
1	1	0	8	10.5	4
5	1	0	6	40	10

The use of H_2O_2 , however, produces results greatly superior in every way to those obtained with the nitric acid alone, but especially so in regard to speed of reaction and excess of acid. Solution occurs so quickly and completely that even small samples can be readily dissolved in a slight excess of acid, it being unnecessary to have a considerable volume of liquid at the start on account of the rapidity of the reaction. The following results indicate the advantages pertaining to the use of H_2O_2 . Practically the same results could be obtained with considerably more dilute acid:—

Sample used. Grms.	Solution mixture.			Total cc. of liquid at start.	Minutes required for solution (approximate).
	Parts HNO_3 .	Parts water.	Cc H_2O_2		
1	1	2	0.5	5	1
3	1	1	1.5	10	1

Hydrochloric Acid.—The action of this acid about parallels that of nitric, or if anything it is somewhat more efficient, for although concentrated hydrochloric is only about one-half as strong as concentrated nitric acid it acts with equal speed. Owing to its lesser concentration a larger volume is required for the same equivalent of acid than with nitric, and it was found that owing to this a smaller excess of hydrochloric could be used for a given sample than is necessary when nitric is employed; e.g., a 5 grm. sample, which was readily dissolved by four times the theoretical amount of hydrochloric acid, required six times the theoretical quantity of nitric acid to effect its solution.

This behaviour with hydrochloric acid was quite unexpected, the writer having always been under the impression that these oxides were practically insoluble in it except in the presence of a reducing agent. The chloride ion apparently acts in the latter role, free chlorine being given

off during the reaction. H_2O_2 acts with hydrochloric acid in exactly the same manner as with nitric.

Acetic Acid.—The acid used contained 99.50 per cent $HCl \cdot H_2O_2$ and proved to be a very unsatisfactory solvent for these oxides. Its action is extremely slow, so that long boiling, with the consequent necessity of a large excess of acid, is necessary in order to obtain the solution of even a moderate amount of material; e.g., a 1 grm. sample was treated with twenty times the required quantity of acid, the mixture heated to boiling, then placed on the steam bath and frequently shaken; after half an hour the residue was filtered off, the filtrate precipitated with oxalic acid, and the oxalates ignited to oxides; this oxide did not exceed more than 0.05 grm. in weight.

Very peculiarly H_2O_2 does not seem to facilitate solution in this case, repeated experiments using large excesses of the peroxide giving no better results than that above noted. As suggested by Dr. W. C. Moore, of the Research Laboratory, this behaviour may be due to some reaction taking place between the hydrogen peroxide and the acetic acid itself.

Summary.

1. This investigation has shown that the cerium group oxides are fairly readily dissolved by sulphuric, nitric, or hydrochloric acid, and especially so when the concentrated acids are used, although in the case of the latter two considerable dilution still permits of satisfactory results being obtained. However, it is necessary to use a considerable excess of the respective acid, and more particularly so if the sample is small and it is required to dissolve it in concentrated acid.

2. Acetic acid was shown to be a very unsatisfactory solvent.

3. The use of hydrogen peroxide makes rapid dissolving of the oxides by a very small excess of sulphuric, nitric, or hydrochloric acid possible even in quite dilute solution. With acetic acid, however, the use of hydrogen peroxide does not produce this favourable result.—*Journal of Industrial and Engineering Chemistry*, viii., No. 3.

ASH TESTS FOR PER CENT OF FILLER IN PAPER.

By JOS. E. PLUMSTEAD.

THE value of ash tests or test for the per cent of filler retained in paper is without doubt recognised to a certain extent by every practical paper-maker. Few paper-makers, however, attach any more significance to an ash test than that the sheet in question has a certain number of pounds of clay, agalite, or other filler per 100 lbs. of paper. Nevertheless it is a fact that tests made at different points through the paper-making process have proven or disproven some of the seemingly unexplainable problems that often confront paper-makers, paper-mill engineers, and chemists.

In a paper-mill chemical laboratory the final result of an ash test of a certain sheet from a particular machine is usually reported as per cent retention of filler, and this result is reached in the following manner:—An average sample of the filler used is drawn in the usual manner, and a small weighed portion placed in a crucible over a blast lamp and ignited to a constant weight, and from these weighings the percentage of volatile matter in the filler is calculated. A weighed sample of the paper to be tested for per cent retention of filler is then taken and ignited in a crucible to a constant weight, and from these weighings the per cent ash in the paper is calculated. From the following formula the amount of filler retained in the paper or the per cent retention by the machine is found:—

$$\frac{Pc}{F-V} = \text{per cent retention by machine.}$$

When—

Pc = Per cent ash in paper sample.

F = Lbs. of filler used per 100 lbs. of paper produced by that machine.

V = Volatile matter in the weight F.

If greater exactness is desired a correction may be made for the ash in the fibre used or in constituents of the paper other than the loading material. This is, however, useless from a practical standpoint.

There are various causes—in the filler itself, in the method of beating, and in the manner of running the paper machine—for a higher or lower percentage of retention in some cases than in others. In the filler qualities which tend to give a higher percentage of retention are a colloidal character, fibrous texture, and large particles. These qualities may be estimated by a chemist's judgment from microscopical comparisons, elutriation, and rate of settling tests and aniline dye absorption tests. The extremes of these qualities may cause almost any variation in the retention of filler. A thoroughly beaten stock will retain much more filler than stock beaten a short time. As high as twenty points of difference between stock beaten three and a-half hours and stock beaten six hours has been noted. There are several ways in which the machine tender may raise or lower the retention of filler. If the machine has a short wire the speed of the machine should be correspondingly slow, otherwise harsher treatment must be resorted to in order to remove the water, and the water will, in being forced through the sheet faster, carry with it more of the filler. The stock should be run to the machine at the heaviest possible consistence, to allow for the most efficient re-use of the rich white water which has been forced through the wire. An escape of the white water means an inevitable drop in the retention. If it cannot all be used to advantage at different points in the process it can be settled and the sludge drawn off and re-used at some point, either in the beater or in the beater stuff chest. The ream weight will largely influence the retention of filler, and this fact should be taken into consideration when comparing ash tests of different sheets; thus, other conditions being the same, the retention of an 80-lb. sheet should be about ten points higher than a 50-lb. sheet.

The writer has found the following method effective in hunting down reasons for seemingly inexplainable low retentions. Convenient portions of stock, about 50 cc., are taken from the beater or beater chest and the flow box and a dry sample from the reel, following as nearly as possible the transit of the stock from one place to the other. The wet and dry samples are then placed in a dry oven and dried to a constant weight, and then ignited and weighed, and the ratio of filler to fibre noted in each case. These tests are repeated several times and the averages taken. The average ratios obtained in this manner are then compared with ratios obtained in the same manner on the same kind of sheet, running on the same machine or on another machine at conditions giving the recognised standard ash test for that sheet. These results should indicate the following things:—

- (1) Whether the required amount of filler was actually furnished to the beater.
- (2) The consistence of the stock going on the wire.
- (3) The comparative loss of filler through the wire.

With the trouble thus definitely located it is a simple matter to remedy the defect.

Occasionally in the run of routine ash tests, when a small furnish of filler has been made per beater, the retention will figure out more than 100 per cent. This trouble can almost invariably be traced to a lack of system in furnishing broke to the beaters, either from furnishing broke in irregular quantities to different beaters of the same machine or furnishing the beaters of one machine with broke from another whose sheet contains a different relative amount of filler. It may be safely stated in the case of routine ash tests of paper of known qualities, if the

retention varies more than five points either way from the average for that sheet that machine trouble will have arisen in 75 per cent of the cases from irregularities in furnishing broke.

The writer has found that when all practicable precautions have been taken to prevent the loss of clay through escape of white water the approximate average retention for best English china clay is as follows:—

10 lbs. china clay used per 100 lbs. paper made should give about 50 per cent.

15 lbs. china clay used per 100 lbs. paper made should give about 90 per cent.

20 lbs. china clay used per 100 lbs. paper made should give about 85 per cent.

This weight is made up of—

Fibres	80 per cent	=	1'2524	grms.
Loading material ..	15 "	"	=	0'2348 "
Animal size	5 "	"	=	0'0783 "
				1'5655 "

And 1 cc. of paper contains—

Fibres	0'783	grm.
Loading material	0'147	"
Animal size.. ..	0'049	"
	0'979	"

As may be seen, in this case the air space amounts to an important part; paper consequently possesses a not inconsiderable specific volume. This is lost in calendaring, while a corresponding increase in the surface does not take place. The strength of the sheet is augmented by increasing pressure, but only up to a certain point, beyond which the strength again decreases. When the pressure in calendaring is too high, therefore, the paper is rendered unnecessarily weak, but consideration for the foremost value, strength, is often not alone determinative; the paper must have a certain finish. The conditions noted have been fortified and confirmed by direct measurements and tests.

The proportion between the weight of the sheet and the volume, which according to the foregoing amounts to 0'979 (consequently the weight of a cc. in grms.), is designated the apparent specific gravity, probably with reference to the air space, and is a dimension to which, certainly not without reason, great importance is attached. According to former suppositions it appears that the thickness of the paper must also be taken into consideration. This readily led to a step further and to the use of the strength of the surface unit of the cross-section as a rule in determining the solidity of a paper. The acceptance of such a standard is, briefly stated, customary in all material tests for similar purposes; also in stating the strength of special fibres. It has, however, obtained no established recognition, but has been superseded, except in England or America, by the generally used tearing strength or breaking length, which, as is well known, is the figure representing the length at which a strip of paper, of the quality under consideration, that is hung up free, tears off at the point of suspension owing to its own weight. The number which—moreover in harmony with the aforementioned cut-surface unit coefficient—has the advantage that it can be used directly, without regard to difference in the grm. weight, is most conveniently obtained with a Schopper apparatus, with a predetermined normal measurement of the strips of 180×15 mm., whereby the average between the results of the machine and the cross-direction (in machine papers) can be decisively given. In the same manner the strength of a single paper, per surface unit of the cross-section, can be given; the question, however, is how far in every instance the accepted breadth and length is perfectly suitable for the test strips. An intelligent investigation may furnish an explanation of this.

In addition to the advantage of a unit of strength,

uniform for different material, in using the section unit we have the certainly not unimportant relation between the specific thickness of paper and its specific strength.

Between the two strength figures there is apparently a close connection. If we typify apparent specific gravity by S , fracture length by L , strength of the paper to the surface unit of the cross-section by K , thickness of the paper (as before) by t , and breadth of the test strip by b , the breaking load for the breadth $b = L \times b \times t + S = K \times b \times t$, that means $L \times S = K$, or the product of the breaking length and the apparent specific gravity is the strength of the surface unit of the section. This proportion has been directly confirmed by careful experimental test in every instance, and such an investigation is instructive and furnishes special knowledge as to the possibility of producing paper of great strength.

The aforementioned factors are the most important in what is known as the C.B.S. units. It would be difficult to predict to what extent the methods of determination indicated will find employment. In part they are only a development and another application of methods already in use, and up to the present time the new method appears to have attracted attention only in its home country. That it merits attention for certain questions, and possesses more than speculative theoretical interest is probably far beyond any doubt.—*Chemical Engineer*, xxiii., No. 2.

THE EXTRACTION AND SEPARATION OF THE RADIO-ACTIVE CONSTITUENTS OF CARNOTITE.*

By H. M. PLUM.

EVER since the discovery of radium by M^{me}. Curie and the announcement of its wonderful properties there has been a very great demand for this element. On account of its scientific interest such extensive investigations have been carried out that the supply of radium at all times has fallen short of the demand. The more recent claim that it has therapeutic value in the treatment of such diseases as cancer has so greatly increased the demand that the study of the radium-producing ores, along with the best methods of extracting the radio-active material, has become extremely important. In view of these facts it can readily be seen that the demand for radium will be on the increase, and that any research which would point out efficient and practical methods for the recovery of this element will be of both scientific and practical value.

This paper presents the results of a critical investigation, carried out under the direction of Dr. Herbert N. McCoy, of various methods of treating carnotite with the object in view of extracting not only uranium, vanadium, and radium, but also its other long-lived radio-active constituents—ionium, Radium D, Radium F, and actinium. It has been established by McCoy (*Ber.*, 1904, xxxvii., 2641), Boltwood (*Nature*, 1904, lxx., 80; *Phil. Mag.*, 1905, ix., 599), and Strutt (*Nature*, 1904, lxi., 473; *Proc. Roy. Soc. (A)*, 1905, lxxvi., 81, 312) that there is a constant ratio between uranium and radium in ores; consequently the ores richest in uranium contain most radium. Among the most important of these ores are pitchblende, autenite, chalcolite, and carnotite. Of these until recently pitchblende has been looked upon as the best source of uranium, the mineral usually containing from 40 to 90 per cent of uranoso-uranic oxide, U_3O_8 . The great demand for the radio-active elements, however, has nearly exhausted the known deposits of this ore.

The main source of supply for uranium at the present time is carnotite. It is a hydrated vanadate of uranium and potassium (Hillebrand and Ransome, *Am. Journ. Sci.*, 1900, x., 120) and usually occurs as a canary-yellow

* *Journal of the American Chemical Society*, xxvii., No. 8.

powder disseminated in sandstone. It does not occur as a rule in a pure state, but as a mixture of minerals containing (in addition to uranium, vanadium, and potassium) varying amounts of silica associated with such elements as barium, calcium, and iron. The principal carnotite deposits are those of Colorado and Utah, where uranium ore is found in far larger quantity than in any other region in the world.

Many of the commercial methods proposed for treating uranium ores, or ores containing both uranium and vanadium, have had as their object the extraction of these elements only, without reference to the recovery of the radium. In such cases the radium has been lost because operators have often not known the methods best suited for obtaining it. A considerable amount of American carnotite has been shipped to Europe. These ores have been purchased mainly for their radium content, and the profit has come largely in connection with the extraction of the radium. Richard B. Moore and Karl L. Kithil (*Bulletin* 70, 1913, U.S. Bureau of Mines, Denver), in a preliminary report on uranium, radium, and vanadium, and Siegfried Fischer (*Trans. Am. Electrochem. Soc.*, xxiv.), in an article on the carnotite industry, have discussed quite fully the principal methods now in use for treating carnotite.

There are two principal methods of attack—acid processes and basic processes. Three of the former may be mentioned: Fleck's method, which consists in leaching the ore with dilute sulphuric acid; Radcliff's (U.S. patent No. 1,049,145, 1913), in which the ore is fused with sodium acid sulphate; and that of Moore and Kithil, who effect a partial solution by treatment with boiling nitric or hydrochloric acid. Among the basic methods, Bleeker's process (U.S. patent No. 1,015,469, 1912) consists of roasting the ore with sodium chloride and sodium hydroxide; Fischer's (U.S. patent No. 986,180, 1911), of evaporating with caustic soda solution and roasting, while Haynes and Engle (U.S. patent No. 808,839, 1905) boil with carbonate of soda.

In most of the recent commercial methods which have had to do with carnotite the investigators have generally been satisfied to find the best means of extracting vanadium, uranium, and radium without regard to the other radio-active elements. In the present work, in addition to the above, the aim has been to follow the other long-lived radio-active elements and to find means of recovering them also.

The ore used in these experiments represented the concentrates from a Colorado carnotite. (This material was furnished by Mr. J. M. Flannery, President of the Standard Chemical Company of Pittsburgh, to whom I wish here to express my thanks for his generosity). It was in a very finely divided form, dark in colour, and had been thoroughly mixed in the process of concentration. This concentrate contained approximately 6 per cent of vanadium, 4 per cent of uranium, and 4 per cent of iron. There were only small amounts of barium and lead in the ore, the barium radium sulphate from one kilogram of carnotite weighing about 7 grms. The rare earths were lacking and very little if any thorium could be detected.

The analysis of the concentrate was made in several ways. The simplest and most satisfactory method consisted in boiling 5 grms. of material with a large excess of concentrated nitric acid for about an hour, by which time complete decomposition had taken place. In case vanadium was to be determined the nitric acid was completely expelled by evaporation to fumes with an excess of sulphuric acid. Water was added, and the whole boiled for some time with a large excess of sodium carbonate solution and filtered. The insoluble residue, consisting of the carbonates and hydroxides of iron, &c., was dissolved in hydrochloric acid and again treated with sodium carbonate solution and filtered, and this filtrate added to the main filtrate. This solution now contained all the uranium and vanadium but was free from iron. It was acidified, boiled to expel carbon dioxide, and made alkaline with sodium

hydroxide (free from carbonate). The uranium was precipitated as yellow sodium uranate, while the vanadium remained in solution as easily soluble sodium vanadate. In case all the vanadium was not present in the pentavalent form, the addition of a little bromine water to the alkaline solution completed the oxidation and rendered the vanadium readily soluble in the sodium hydroxide, thus giving an easy and complete separation of the former from the uranium. The precipitate of sodium uranate was dissolved in sulphuric acid, reduced with zinc, and titrated with standard permanganate (McCoy and Bunzel, *Journ. Am. Chem. Soc.*, 1909, xxxi., 367). The mean of concordant analyses was 4.27 per cent uranium. Vanadium was determined in the filtrate from the sodium uranate by acidifying with sulphuric acid, boiling to expel bromine, reducing with sulphur dioxide, and then titrating with standard permanganate after freeing the solution from the excess of sulphur dioxide. The average of the results gave 5.5 per cent vanadium.

The total activity of this ore was calculated from the percentage of uranium it contained. According to the method used by McCoy (*Phil. Mag.*, 1906, ii., 176) 1 grm. of an ore containing 4.27 per cent of uranium, made into a very thin film, should show a total α -ray activity 194 times our standard, which was a thick film of U_3O_8 of 35.41 sq. cm. area. The distribution of this activity, as calculated from the ranges of the radio-active elements on the assumption (McCoy and Viol, *Ibid.*, 1913, xxv., 357; McCoy, *Phys. Rev.*, 1913, i., 401) that the intensity of activity is proportional to R^3 (R =range), gave the following results for 100 grms. of our ore, for which the total activity should be 194 times that of the U_3O_8 standard:—

Element.	Range.	Calculated activity (Ra = 1).	Distribution of activity from 100 grms. ore.
Uranium 1	2.50	0.831	36.3
Uranium 2	2.90	0.917	
Ionium	3.00	0.938	19.5
Radium	3.30	1.000	105.5
Radium Em	4.16	1.170	
Radium A	4.75	1.275	
Radium C	6.94	1.640	
Radium F	3.77	1.090	22.6
Actinium and its active products.. ..			11.0
Total			194.9

The activity of actinium was calculated from Boltwood's determination of the activity due to actinium in uranium minerals (*Am. Journ. Sci.*, 1908, xxv., 269). The above figures were used as the basis for finding the percentage of recovery of the different radio-active elements in the experiments carried out in this work. In the case of uranium, however, the percentage of recovery of that element was found directly by analysis, while with radium the determination of the amount of emanation present gave the most satisfactory results. To get the activity of radium the emanation liberated by fusing samples of the material to be tested with anhydrous potassium acid sulphate was collected and then measured in an emanation electroscope, after the manner described in a later paragraph. The activity of polonium was determined by depositing it on copper (Marckwald, *Phys. Zeit.*, 1903, iv., 51; *Ber.*, 1903, 2662) and then comparing the activity with that of the standard uranium film. In the case of ionium, where the final residue containing it was very small, the material was dissolved, and thin films, satisfactory for α -ray measurement, obtained from the deposit left by evaporating portions of this solution. The activity of the radio-lead and actinium was determined by thin films made in a manner similar for those used for measuring the activity of the original ore, the final measurements being made after the films were a year old.

(To be continued.)

THERMOMETERS IN DISTILLATION FLASKS.

THE Bureau of Standards of the U.S. Department of Commerce has just issued Technologic Paper No. 49, entitled "The Emergent Stem Correction for Thermometers in Oil Distillation Flasks."

Complex mixtures of hydrocarbons of different chemical composition are separated into simpler fractions by fractional distillations carried out between definite temperature limits. Such distillations are carried out in laboratory tests in several different forms of flasks, in which the temperature limits fixed by the specifications are measured by mercurial thermometers, the stems of which project out of the flask into the room, and thus cause the thermometers to read too low—i.e., lower than they would read if the bulb and stem were all at the temperature of the oil vapour around the bulb. To find the true temperature of the vapour it is therefore necessary to apply a so-called stem correction to the observed reading of the thermometer. In the paper above referred to these stem corrections have been determined for several different forms of distillation flasks, and it is shown that in oil distillation tests carried out in the interval 200° to 300° C. it may amount to over 15° C. (27° F.), and it is shown that different chemists fractionating the same oil will find quite different results if one applies the stem correction and another neglects to do so.

The paper also gives a very simple method by which the chemist can determine the total correction that he must apply to the observed reading of his thermometer to find the true temperature of the vapour in the flask—i.e., the total correction due to scale error and to emergent stem. The method consists in reading the thermometer when naphthalene is boiled in the flask, and again when anthracene is boiled in the flask. The boiling point of the former has been found to be 218° C. and of the latter 340° C. The amount by which the observed thermometer readings differ from these two temperatures gives the total correction to the thermometer at two points on its scale, and corrections at intermediate points can be found by interpolation.

Copies of this paper may be obtained without charge upon application to the Bureau of Standards, Washington, D.C.—*Chemical Engineer*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 6, 1916.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of John Frederick Alder (died March 18, 1916), and Cecil Hamersley Waldron (killed in action, March 2, 1916).

The PRESIDENT announced that the Council have appointed the following Committees for the year 1916–1917.

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, Sir Edward Thorpe, Sir William A. Tilden, and the Officers.

House Committee—Messrs. Horace T. Brown, R. Messel, J. E. Reynolds, J. M. Thomson, Sir William A. Tilden, and the Officers.

Library Committee—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, T. M. Lowry, J. M. Thomson (Chairman), Sir William A. Tilden, J. A. Voelcker, the Editor, and the Officers.

Publication Committee—Messrs. A. C. Chapman, F. G. Donnan, B. Dyer, A. Harden, T. M. Lowry, F. L. Pyman, G. Senter, J. F. Thorpe, and the Officers.

Research Fund Committee—Messrs. W. R. Bousfield, Horace T. Brown, Sir James J. Dobbie, F. G. Donnan, H. J. H. Fenton, P. F. Frankland, A. Lapworth, W. H. Perkin, J. F. Thorpe, W. P. Wynne, and the Officers.

The PRESIDENT announced that the Council had decided that an Extraordinary General Meeting of the Fellows should be summoned for Thursday, May 11, 1916, at 5 p.m., to consider the question of the removal of the names of the nine alien enemies from the list of our Honorary and Foreign Members.

A notice convening this meeting will be issued to the Fellows in due course.

Certificates were read for the first time in favour of Messrs. Ganesh Sakharan Agashe, M.A., M.Sc., Pachaiyappa's College, Madras, India; Percy Herbert Clifford, The Acacias, Hillingdon, Middlesex; John Harbourn Cooke, B.A., Dungarvan, Co. Waterford; Thomas Bertram Henderson, 44, Dene View, Wallsend-on-Tyne; George James, 56, Cranworth Street, Chorlton-on-Medlock, Manchester; Frank Charles Laxton, High Street, Ely; Frederick Owen, 16, Brooke Street, Bradford, Manchester; Maurice Ernest Probert, Trevine, Hadley Road, New Barnet.

The following Certificate has been authorised by the Council for presentation to ballot under By-law I. (3):—Nowrosji Maneckji Bhathena, Mazagon, Bombay, India.

Dr. ALEXANDER SCOTT delivered his Presidential Address, entitled, "Our Seventy-fifth Anniversary."

A vote of thanks to the President for his Address, coupled with the request that he would allow it to be printed in the *Transactions*, was proposed by Prof. J. MILLAR THOMSON, and seconded by Sir JAMES J. DOBBIE, the President making acknowledgment.

Research Fund.

A meeting of the Research Fund Committee will be held in June next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Thursday, June 1, 1916.

All persons who received grants in June, 1915, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Honorary Secretaries not later than Thursday, June 1.

The Council wish to direct attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

PHYSICAL SOCIETY.

Ordinary Meeting, March 24, 1916

Prof. C. VERNON BOYS, F.R.S., President, in the Chair.

A PAPER entitled "*The Laws of Variation of Resistance with Voltage at a Rectifying Contact of Two Solid Conductors, with Application to the Electric Wave Detector*," was read by Mr. D. OWEN, B.A., B.Sc.

The paper contains an account of an investigation, the primary object of which was to determine the nature of the physical actions occurring at a rectifying contact. Resistance characteristics are given for various contacts, some including a mineral, some in which both elements are metals. It is shown that a specific characteristic may be drawn for any given pair of materials. The experimental results are in accordance with the view that the actions are thermo-electric, the main determining factors being the thermo-electric power and the temperature-co-efficient of electric resistance.

Based on the law of constancy of the voltage co-efficient calculations are given showing the best value of the re-

sistance of the telephone in a wireless receiving circuit in which the contact detector is employed. The influence of a polarising voltage is also traced.

The use of the combination of rectifier with a direct-current galvanometer as indicator of the balance point in an alternating-current bridge is examined, and it is shown that the minimum detectable alternating voltage cannot be reduced much beyond a millivolt.

DISCUSSION.

Mr. DUDELL thought the paper was a very important contribution. He had no definite opinion as to the true explanation of rectifying contacts. In practice very much depends on the exact part of the crystal at which contact is made. With regard to thermo-electric forces, he had examined a large number of crystals in the hope of obtaining contacts which were more stable than those ordinarily employed, and he had concluded that no mineral which did not show thermo-electric effects was of any use as a detector. There might be exceptions in the case of metals, but the rule applied to all sulphides. His experience with regard to the receiving telephone differed somewhat from the author's. In a telephone the resistance and impedance depend on the frequency. In practice it seemed desirable to keep the impedance of the telephone of the same order as the resistance of the detector, and adjust the latter until the desired sensitivity is attained. In receiving strong signals one may employ very tight contacts in which it appears to be impossible that there should be any air film. A satisfactory rectifying action is still, however, obtained.

Prof. G. W. O. HOWE thought that it was well to avoid flying off to new hypotheses in order to explain new phenomena if they could possibly be accounted for on well-known grounds. He was pleased to see that the author had been able to explain rectifying contacts without invoking any mysterious new properties. He was rather surprised to gather from the author's remarks that the thermo-electric theory was generally discredited. His impression had been that the work of Dr. Eccles had established it as the accepted explanation. Had any of the exponents of the electron theory attempted to give a detailed explanation of the observed phenomena on that basis? What was the origin of the "settling down" of contacts mentioned by the author? Was it a mechanical or thermal effect? He would like to hear just in what respect the results of Mr. Owen's work differed from those of Dr. Eccles.

Dr. W. ECCLES remarked that he was glad to find such agreement on the absurdity of rushing to special explanations of these phenomena. Certain workers had thought that electrostatic attraction altered the area of contact. Others assumed the opening of trapdoors to let electrons through, the mechanism of the process being considerably more difficult to explain than the original results themselves. Prof. Fleming had found that many of the substances used as detectors were photo-electric—i.e., they give off electrons under the action of light—and he assumed that rectifying phenomena were caused by a similar action of the longer electro-magnetic waves. He (Dr. Eccles) had tried to put these points straight by explaining the phenomena in terms of well-known physical properties, such as the resistance coefficient, Peltier effect, &c., and had found it possible to account for all the effects. The theory proved unpopular because it had nothing occult about it. Mr. Owen had dropped the Thomson effect from his treatment. He thought this was not justifiable, as the Thomson effect was a physical fact which must enter into the result in practice. Leaving it out of consideration simplifies the treatment, but loses the explanation of several of the erratic properties of detectors. For instance, the theoretical resistance characteristic curves obtained by Mr. Owen are parabolic. It is obvious, however, that the experimental curves are of the fourth degree. The Thomson effect must be introduced to explain the way the curve bends off at the extremities. One important result of the author's was that for the same

materials the value of R_m/R_0 was constant for any contact, light or heavy. This appeared to him to be due to the fact that increasing the area of contact by increasing the pressure was equivalent to putting two or more similar contacts in parallel.

Mr. A. F. HALLIMOND (communicated)—I should like to congratulate the author on his reduction of the curves for each contact-pair to a specific resistance characteristic. If it is found that the same process can be employed in all cases a very useful and simple means of comparison will be established. The result seems the more remarkable in being based upon the resistant-curves, and I should like to ask whether the relation throws any light on the conditions obtaining at the contact when the pressure is varied. With reference to the heating of the contact, I believe that Prof. Pierce observed that at 80 cycles no lag occurred, such as might be due to heating. The author's arrangement by which the current may pass from 0.003 second would seem to be even more sensitive. Was any variation observed in the resistance with the time of passage of the current? With regard to the thermal effects, might I suggest the investigation of pyrite, a mineral in which adjoining areas may exhibit widely different thermal E.M.F.'s?

The AUTHOR (in reply) said he was glad to learn that it was Mr. Duddell's uniform experience that high thermo-electric power and sensitiveness of a contact detector go together. In regard to the relation of impedance of telephone to the resistance of the contact he was quite prepared to find that the conclusions deduced from the simple treatment employed in the paper required modification to conform to the actual conditions of practice. In reply to Prof. Howe's inquiry as to the cause of the "settling down," this was not due to thermal action; the small testing voltage was applied only at intervals, and was not itself the cause of the change described. The effect appeared to be of the nature of an adjustment of the molecules bounding the contact when their setting was changed; it was probably allied to the slow changes met with in the study of elastic strains. He did not go so far as to say that the thermo-electric theory had become generally discredited, but rather that it stood in need of confirmation. He would endeavour briefly to point out in what relation his own work appeared to stand to that of Dr. Eccles; this reply would cover some points of difference which Dr. Eccles had commented upon. Dr. Eccles employed coefficients representing the Peltier effect, the Thomson effect, and the temperature coefficient of resistance. The author finds that the existence of softening and consequent increase of area of contact due to rise of temperature becomes very important at the higher voltages. This effect is complicated and thus not amenable to mathematical treatment; the course adopted in the present paper is, therefore, to restrict the application of the formulae within small limits of voltage—say, a few tenths of a volt. Apart from this, the chief point of difference is in the emphasis laid on the relative value of the coefficients. The author finds that the experimental results in the case of all the mineral and metallic contacts tested may be explained without invoking the Thomson effect; the conclusion is, therefore, drawn that this term is of small importance in comparison with the Peltier effect, at all events at low voltages. It thus fortunately becomes possible to simplify the theory appreciably. Again, in the author's view not only does resistance admit of more precise measurement, but the statement of results in the form of resistance characteristics brings out the essential features of the behaviour of these contacts more clearly than if current characteristics are employed. In reply to Mr. Hallimond, the determination of resistance of contact as a function of pressure is not specially considered in the paper. The tests here recorded tend, however, to show that pressure only enters in so far as it alters the area of contact. In regard to the question of time-lag, this is the subject of experiments now in progress. In reference to pyrite, the author fully grants that heterogeneity may and

does exist in this and other cases; for further instance, in the high and low-resistance specimens of carborundum referred to in the paper, both possessing high thermo-electric power, but of opposite signs in the two cases.

A paper entitled "*The Electrical Capacity of Gold-Leaf Electroscopes*," was read by Dr. T. BARRATT, A.R.C.S.

A gold-leaf electroscope is frequently used to compare exceedingly small ionisation currents. For this purpose it is much more sensitive than a quadrant electrometer. If the capacity of the electroscope is known, then the absolute value in amperes of the ionisation current can be deduced. A method is described for measuring the capacity of a gold-leaf electroscope, the method depending on sharing the charge of a parallel plate air condenser of measurable capacity as many times as necessary, and deducing the capacity of the electroscope from the observed drop of potential. The method gives consistent results when the experimental conditions are widely varied. The amount of deflection of the leaf appears to have little influence on the result.

On account of the lateness of the hour, the paper was not opened for discussion. Several Fellows communicated remarks to the author, and these, together with his reply, will appear in the *Proceedings*.

ROYAL INSTITUTION. *Annual Meeting, May 1, 1916.*

The DUKE OF NORTHUMBERLAND, K.G., President,
in the Chair.

THE ANNUAL Report of the Committee of Visitors for the year 1915, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Report of the Davy Faraday Research Laboratory Committee was read. Fifteen new Members were elected in 1915. Sixty-two Lectures and Nineteen Evening Discourses were delivered in 1915. The books and pamphlets presented amounted to about 276 volumes, making with 527 volumes (including periodicals bound) purchased by the Managers, a total of 803 volumes added to the Library in the year. Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Col. Edmond H. Hills.

Managers—Sir Thomas Barlow, Bart., Sir William Phipson Beale, Bart., Dr. Horace T. Brown, Sir James Mackenzie Davidson, the Right Hon. Lord Grenfell, Charles Hawksley, Col. Sir Frederick Nathan, the Hon. Richard C. Parsons, Sir James Reid, Bart., Sir Napier Shaw, Alexander Siemens, Silvanus P. Thompson, The Right Hon. Lord Wrenbury, Sir Alfred F. Yarrow, Bart., The Hon. Sir Robert Younger.

Visitors—Horatio Ballantyne, Sidney George Brown, John F. W. Deacon, William Duddell, Lieut.-Col. Henry E. Gaultier, Dr. J. Dundas Grant, John W. Jarvis, H. R. Kempe, Francis Legge, Ernest R. Moon, Henry G. Plimmer, Sir William Wyndham Portal, Bart., Alfred W. Porter, Hugh Munro Ross, Joseph Shaw.

Radium In Japan.—Dr. Ishidzu, of the Tokyo Hygienic Laboratory, has been investigating the hot and mineral springs of Japan with a view to ascertain the quantities of radium which they contain. It is reported that, as a result of his investigations, he considers Japan to be the richest radium country in the world. Considerable proportions of radium are declared by Dr. Ishidzu to be present in the waters of a mineral spring in the Yamanashi Prefecture, and radium-bearing water also occurs in another spring at Chuggoka.

NOTICES OF BOOKS.

A System of Physical Chemistry. Vols. I. and II. By WILLIAM C. MC. LEWIS, M.A. (R.U.I.), D.Sc. (Liv.). London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1916. Pp. xiv. + 523; vii. + 552. Price 9s. per volume. (Sold separately).

THE wide scope of this text-book and the prominence given in it to recent work combine to make it a valuable addition to the series of Text-books of Physical Chemistry edited by Sir William Ramsay and a particularly interesting contribution to scientific literature. The author has collected his material from all sources, and has produced a work which, while ambitious in design, has the obvious advantage of having been compiled with one aim in view and one leading thought in the mind. The system adopted is that of considering the phenomena of chemical equilibrium successively under three heads—firstly, from the kinetic standpoint, secondly, from the thermodynamical point of view, and thirdly, from that of the new statistical mechanics. The first of these is treated in Volume I., which is certainly by far the easier and more interesting. Although very wisely no attempt has been made to veil difficulties or to avoid the employment of mathematics when necessary, this volume is more descriptive in character than the second, and contains admirable accounts of experimental work. At the beginning, recent work on the reality and magnitude of the molecules is described, often in the very words of the original investigators, and the student is certain to find absorbingly interesting the history of the different methods of attack adopted by various workers, which are all very lucidly explained in considerable detail. In the second volume, in which thermodynamics is first treated, a large amount of mathematical analysis is unavoidable, and it seems probable that even the previously well-trained student will find his powers taxed in order to cope with it. A comparatively short section on radiation chemistry and the theory of radiant energy constitutes the second part of Volume II., and will probably come as a decided relief after the stiffer reading of the first part. The book is one of considerable value for students who already have some knowledge of physical chemistry, and is highly to be commended for the attention paid in it to the latest developments of the science.

Wireless Time Signals. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1915.

THIS authorised translation of the official handbook, "*Réception des Signaux Radiotélégraphiques pour la Tour Eiffel*," issued by the Paris Bureau of Longitudes, will be valued by navigators and others who are interested in wireless telegraphy. It contains a simple exposition of the principles of radiotelegraphy, in which a clear and practical explanation is given of different types of detectors, receiving apparatus, and methods of making adjustments. This is sufficiently non-technical to be readily understood by amateurs, and is fully illustrated by diagrams and plans. The methods and apparatus used at the Eiffel Tower installation is described in detail and the organisation of the service is discussed, while a chapter is included on the methods of calculating comparisons. Appendices have been added by the translators on the weather signals and on International Time Signals.

Saving Fuel in Heating a House. By L. P. BRECKENRIDGE and S. P. FLAGG. Technical Paper 97. Washington: Government Printing Office. 1915.

THIS technical paper deals with the selection, care, and operation of different apparatus for heating houses, the aim being to put before the public definite suggestions as

to the best methods of effecting economy of fuel. Tabular summaries are given of the advantages and disadvantages of various fuels and electricity, and different methods of heating—fireplaces, various kinds of stoves, hot water systems—are discussed. The authors' statements and conclusions are naturally chiefly applicable to conditions in America, but many suggestions of value to the British public will be found in the sections on the factors governing the consumption of fuel and on the firing of different kinds of fuel. An interesting item is the record of the fuel consumed in a season in heating a residence, of which particulars as to size, location, &c., are given.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii. No. 10, March 6, 1916.

New Reaction of Urine.—A. Bach.—The author has already shown that the reduction of nitrates and colouring matters in animal tissues is due to the simultaneous intervention of a ferment and a co-ferment which, taken separately, do not exercise any reducing action. In fresh milk this ferment exists unaccompanied by its co-ferment, and produces, either with the help of the co-ferment obtained from the tissues or with the help of aldehydes, the same phenomena of reduction as are observed in the tissues. The co-ferment can be extracted from the tissues by means of boiling water. It is found in commercial peptones and also in albumens completely degraded to amino acids. Normal urine contains appreciable quantities of the same co-ferment; that is to say, that nitrates are not reduced to nitrites by it alone, but in presence of the ferment contained in fresh milk it does reduce them. As the nitrites formed can easily be determined the reaction may be useful in physiological and pathological researches. To perform the estimation 15 cc. of the fresh urine, 10 cc. of fresh milk, and 1 gm. of sodium nitrate are heated together to 60° for twenty minutes. At the same time a blank test is prepared containing the milk and urine without the nitrate. To each solution 0.5 gm. of finely powdered subacetate of lead is added, and the solution is shaken and filtered. The nitrite is determined colorimetrically in 20 cc. of the filtrate, as in water.

No. 11, March 13, 1916.

Mechanism of Reactions in Aqua Regia.—E. Briner.—Although aqua regia has been known and used since the eighth century very little attention has been paid to the mechanism of its reactions. The chief aim of the present work was to establish the reversibility of the reaction $\text{HNO}_3 + 3\text{HCl} = \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$. From recent observations it might be foreseen that when reacting in a closed vessel the acids would give rise to a liquid phase containing NOCl and Cl_2 co-existing in equilibrium with the aqueous phase. This has been proved experimentally to be the case. In order to ascertain the conditions of equilibrium the author has constructed a series of glass apparatus provided with a compressed air manometer and an electromagnetic agitator, and containing different proportions of the acids of varying concentrations. It was thus proved that the pressure was the same in all the apparatus, and within the limits in which the author worked the system is monovariant, having three phases and two independent components. If the acids are too dilute the liquefied gas phase does not exist, and the pressures decrease as the dilution increases. The reaction is

endothermic, and in order to encourage the liberation of chlorine it is best to raise the temperature, the heating being stronger the more dilute the acids. When the two acids are mixed it is found that the temperature first rapidly rises some degrees and then slowly descends, remaining about 2° below their temperature before mixing, which proves that heat is absorbed during the reaction. The rise of temperature at the beginning is due to the action of the HCl upon the water of the solution of HNO_3 , the heats of solution and dilution of this acid being low in comparison with those of HCl. It was found that when some drops of water, representing the water contained in the solution of HNO_3 , were added to a solution of HCl the temperature rose about 5°.

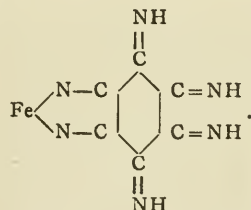
Manganese in Springs of Pyrenees Range.—F. Jadin and A. Astruc.—There is a certain relation between the amount of manganese contained in a water and the total mineral matter in it. Ferruginous waters generally contain a large proportion of manganese. Although waters containing sodium sulphide are usually very poor in manganese the algae growing round it contain a fairly large amount of this element. This is a new proof of the extremely wide diffusion of the manganese in nature and of the essential part it plays in biological phenomena.

Bulletin de la Société Chimique de France.

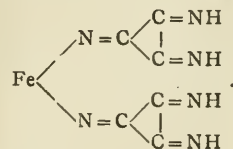
Vol. xix.-xx., No. 3, 1916.

New Constitution Formulæ of Ferro-cyanogen Compounds.—G. Denigès.—Etard and Bémont suggested for the ferrocyanides a cyclic formula represented by

$\text{Fe} \begin{cases} \text{N}=\text{C}-\text{C}=\text{NR}'-\text{C}=\text{NR}' \\ \text{N}=\text{C}-\text{C}=\text{NR}'-\text{C}=\text{NR}' \end{cases}$, while Friedel suggested a similar scheme, giving it in the case of hydroferrocyanic acid the form—

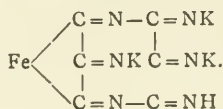


He expressed some doubt as to the validity of this and the corresponding formula for hydroferricyanic acid, pointing out that they would involve the possibility of passing from these compounds to those of the benzene series. Moreover, these formulæ take no count of the fact that in these salts the ordinary reactions of iron are masked, while the other metals which they contain are labile and ionisable. In the hexagonal formulæ the metals, including iron, have the same atomic bonds, and this difference of properties is absolutely inexplicable. The same objection applies to Browning's formula for hydroferrocyanic acid,—

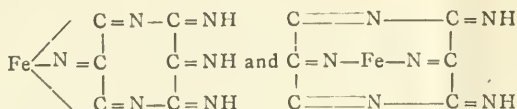


Moreover, these formulæ provide no interpretation of many other facts which Etard and Bémont's work has brought to light. Miolatti has proposed to abandon all constitutional formulæ for these salts, and suggests that they should be included in Werner's general theory of complex salts. Then in the ferrocyanide series in which the iron is

divalent the general formula would be $\text{FeCy}_2 + n\text{CyK}$; in the ferricyanide series it would be $\text{FeCy}_3 + n\text{CyK}$, and in the ferricyanide series $\text{FeCy}_4 + n\text{CyK}$. The author, regarding it as strange that a complete group of carbon derivatives should be incapable of graphic representation, suggests the following scheme for potassium ferrocyanide, for example,—



Here iron having carbon bonds quite different from the nitrogen bonds of potassium would naturally have a different degree of stability in the molecule. Many of the reactions of these compounds can be explained on the basis of this scheme; for example, the decomposition *in vacuo* of potassium ferrocyanide on heating to give Williamson's salt. Also the action of pyrolysis on hydroferrocyanic acid and on ammonium ferrocyanide, and the formation of compounds of the alkaline ferrocyanides and ammonium salt, such as Bunsen's salt, $\text{FeCy}_6(\text{NH}_4)_2 \cdot 2\text{ClNH}_4$. Hydroferri- and perhydroferri-cyanic acids would be respectively:—



MISCELLANEOUS.

University of London, University College (Session 1915-16).—The following Public Lectures will be delivered:—"The School of Chemistry at University College: Turner, Graham, Williamson, Ramsay," by Prof. J. Norman Collie, Ph.D., LL.D., D.Sc., F.R.S., on Tuesday, May 9, at 5 p.m. "The Manufacture of Nitrates from Air by Electric Power," by E. Kilburn Scott, M.I.E.E., A.M.Inst.C.E., on Monday, May 15, at 5.30 p.m. "The Role of Chemical Science in Civilisation," by Prof. F. G. Donnan, M.A., Ph.D., F.R.S., on Tuesday, May 16, at 5 p.m. The Right Hon. Lord Moulton, K.C.B. F.R.S., will preside.

Qualitative Determination of Cadmium.—Roberto Salvadori.—To determine cadmium by means of ammonium perchlorate excess of ammonia is first added to the nitric solution of the sulphates of copper, cadmium, and bismuth precipitated in the second group. The hydrate of bismuth is separated by filtration, and an ammoniacal solution of ammonium perchlorate is added in slight excess to the blue solution. The cadmium is thus precipitated as tetrammonium perchlorate, $\text{Cd}(\text{ClO}_4)_2 \cdot 4\text{NH}_3$, in the form of a white crystalline powder. The precipitate is dissolved on warming, but reprecipitated in the crystalline form on cooling. In presence of copper salts the precipitate forms slowly, and the blue solution sometimes makes it a little difficult to detect the turbidity.—*Annali di Chimica Applicata*, v., No. 102.

Detection in Butter of Foreign Colouring Matter.—A. Bianchi.—When the residue obtained by extracting butter with methyl alcohol is treated with concentrated sulphuric acid a red or crimson coloration is gradually produced; concentrated nitric acid turns the yellow residue brown, while concentrated hydrochloric acid slowly produces a pink coloration. The author has examined the colorations produced by the same three acids with foreign colouring substances extracted from pure butter, and has

collected the results of his investigations in a table from which the following extracts may be made:—With annatto concentrated H_2SO_4 gives a green coloration, turning blue and finally violet; concentrated HNO_3 gives a transient blue which turns yellowish green and then disappears altogether; concentrated HCl produces no change. With saffron, H_2SO_4 gives a dark blue, turning reddish violet and then brownish red. HNO_3 produces a blue and finally reddish colour; HCl no change. With aniline yellow no change is produced with any of the acids. With the help of the author's table the presence of any common colouring matter can be indicated, and in doubtful cases may be confirmed by the usual tests.—*Annali di Chimica Applicata*, v., No. 102.

Direct Quantitative Determination of Carbon Monoxide in Mixtures containing Unsaturated Hydrocarbons.—A. Piva.—The determination of unsaturated hydrocarbons in presence of carbon monoxide by means of bromine water is affected by a considerable error which is greater the greater the concentration of CO in the mixture. The author has now worked out a method by which the monoxide can be determined independently of the presence of unsaturated hydrocarbons. He has found that it is absorbed quantitatively by soda lime at 230° , and that the absorption is rapid enough to be used as a direct method of determination in mixtures of common gases (oxygen, carbon dioxide, unsaturated hydrocarbons, hydrogen, methane). The oxygen and carbon dioxide are first absorbed by potassium pyrogallate or sodium hydrosulphite at the ordinary temperature, and when the volume has become constant the gases are passed over soda lime at 230° , when the diminution of volume gives the amount of CO present.—*Annali di Chimica Applicata*, 1916, v., 82.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.—Biochemical Society, 5.30. (In the Physiological Laboratory, University of London).
— Royal Institution, 5. (General Meeting).
— Royal Society of Arts, 4.30. (Cantor Lecture).
"Vibrations, Waves, and Resonance," by J. Erskine-Murray.
- TUESDAY, 9th.—Royal Institution, 3. "Chinese Painting," by Laurence Binyon.
— Parady Society, 8. "Analysis of the Theory of Gels as Systems of Two Liquid Phases," by E. Hatzchek.
"Properties of Solid Solutions of Metals and of Inter-metallic Compounds" and "Annealing of Metals," by F. C. Thompson. "Changes in the Physical Properties of Aluminium with Mechanical Work—II., Specific Heats of Hard and Soft Aluminium," by F. J. Brislée. "Note on the Annealing of Aluminium," by R. Seligman and P. Williams. "Grain Size Measurements and Importance of such Information," by Z. Jeffries. "Contribution to the Theory of Solution," by E. J. Hartung.
- WEDNESDAY, 10th.—Royal Society of Arts, 4.30. "Neutral Merchants and the Rights of War," by Sir Francis Taylor Pigott.
- THURSDAY, 11th.—Royal Institution, 3. "Flint and Flint Implements," by Sir Pay Lankester.
— Royal Society, 4. Election of Fellows. "Seventh Memoir on the Partition of Numbers—A detailed Study of the Enumeration of the Partitions of Multipartite Numbers," by Major P. A. MacMahon. "Occurrence of Gelatinous Spicules and their Mode of Origin in a New Genus of Siliceous Sponges," by A. Dendy. "Classification of the Reptilia," by E. S. Goodrich. "Experimental Production of Congenital Goitre," by R. McCarrison.
- FRIDAY, 12th.—Royal Institution, 5.30. "Vulgarity," by Dr. A. C. Benson.
— Physical, 5. "Latent Heats of Fusion of Metals and the Quantum Theory," by H. S. Allen. "Lenses for Light Distribution" and "Choice of Glass for Cemented Objectives," by T. Smith.
- SATURDAY, 13th.—Royal Institution, 3. "X-rays and Crystals—First Results and their Applications," by Prof. W. H. Bragg.

THE CHEMICAL NEWS.

VOL. CXIII., No. 2946.

X-RAYS AND CRYSTAL STRUCTURE, WITH SPECIAL REFERENCE TO CERTAIN METALS.

MAY LECTURE OF THE INSTITUTE OF METALS, BY
PROF. W. H. BRAGG.

ON the occasion of the sixth annual May Lecture of the Institute of Metals, delivered on May 4, at a meeting of the Institute in London, Prof. W. H. Bragg, D.Sc., F.R.S. (Nobel Prizeman), gave an interesting account of the new method of applying the properties of X-rays to the study of crystal structure, including the structure of certain metals.

The method, it was shown by the Professor, results in the determination of the exact relative positions of the atoms of which the crystal is composed. It is not successful in every case as yet, because of the lack of practice and experience of the experimenters in the new field and because some of the interpretations are not fully understood. There is no lack of indications; but we are not yet fully aware of the meaning of all of them.

It is natural to attack first such crystals as have an obviously simple structure and consist of few elements associated in simple proportions. It is also of great advantage if the crystals belong to a group of isomorphous members, such as the rock-salt series. This series, in fact, has everything to recommend it to the experimenter—its form is simple, that of the cube; its symmetry is high; it contains two elements only, in equal proportions, *e.g.*, sodium or potassium associated with chlorine or iodine; and there are several members of the series, so that we can watch the effect of changing one element at a time. The constitution of this series was, therefore, one of the first to be examined and made plain.

The constitution of the diamond, which has also been determined, presented a rather more difficult task, because the arrangement of the atoms is not so simple as that of the rock-salt series; although its form is cubic, its symmetry is high, and it contains atoms of one kind only.

Of the metals which will naturally be of especial interest to the Institute of Metals, silver and copper, and by inference gold, have been shown to possess a very simple structure, in which the atoms are arranged as in the piling of shot. Bismuth and antimony have a distorted arrangement; but these two, as well as zinc, have not been completely determined. A beginning had been made with iron. The war has, however, stopped all work of the kind on this metal.

This new field of research, according to Prof. Bragg, depends on a principle already known. When a regular train of waves falls upon a surface separating two media, part is reflected and part goes on. If the part that goes on meets another separating surface, a second portion is reflected and some of this emerges from the second medium in the same direction as the beam reflected from the first surface. It will happen in general that the two reflected beams are out of phase and to that extent destroy one another. Whether they do so or not depends upon the relation between the wave-length, the angle of the inclination of the beam to the reflecting surfaces, and the distance between the surfaces. In this way are explained the colours of the soap film, of the thin layer of oil on the surface of a liquid, of the colours of steel when being tempered, and so on.

If the reflecting surfaces are many in number, not two, the effect is made more intense and at the same time more precise. It occurs in the beautiful colours of potash

crystals as shown by Lord Rayleigh. These crystals are formed of alternating layers, twinned across their surfaces of separation, and for some obscure reason the thickness of all the layers is the same though it varies from crystal to crystal. When white light containing all wave-lengths is incident upon such a crystal, at a certain angle, then only that wave-length is reflected for which the proper relation between the wave-length, angle, and spacing holds good. If the angle is altered the wave-length which is reflected is no longer the same. Hence the beautiful play of colours which the crystal shows.

It is an essential cause of the success of this wonderful effect that the wave-length and the spacing are not very different in amount.

We now pass on to the case of the X-rays. These consist of waves—so, indeed, these very experiments tell us—which are something like ten thousand times shorter than the wave-length of light. To obtain the parallel effect we must look for reflecting surfaces which are ten thousand times closer together than the twinning surfaces of the chlorate of potash crystals, and these are separated from one another by only the forty-thousandth of an inch or thereabout. These also nature has provided in the layers of atoms in the crystal.

It may seem curious that a layer of atoms should act as a reflecting surface: but after all it is not necessary that such a surface should be continuous. A row of iron railings, for example, can act as a reflector of sound waves. A natural face of a crystal contains, no doubt, a layer of atoms arranged regularly; and behind the natural face are other layers all similar, and placed at regularly increasing distances behind it. Thus, all the conditions for this peculiar reflection experiment are present, and we actually find that when a pencil of X-rays of a definite wave-length are allowed to fall upon the face of the crystal, and the crystal is gradually turned round so as to alter the angle of incidence, the reflection of the beam as a whole is non-existent, except when the angle is right. Then it flashes out strongly. When this angle is observed, the relation of the wave-length to the spacing is known.

The instrument used is called the X-ray spectrometer. It has no lenses because X-rays cannot be refracted, and the rays are invisible, so that in place of the telescope appears a chamber containing gas, which is ionised by the X-rays. The resulting electrical effect is observed in an electroscope. It is important that the measurement of the result is quantitative, so that in this respect the new spectrometer has an advantage over the old.

In this way, if we use always the same X-ray, we can compare the spacings between the layers parallel to one after another of the natural faces parallel to the crystal; and in this way we arrive finally at the crystal structure. The instrument is not at all difficult to use, and the observed effects are large and precise, so that it is quite easy to get numerical results. The interpretation is not always quite so easy. One part of it comes readily, *viz.*, the number of molecules to each unit of the pattern of the crystal—the unit being the smaller part, which, being reflected again and again without alteration of orientation or distance from its neighbours forms the complete crystal. For instance, the unit of pattern of potassium sulphate contains four molecules; the unit of pattern of antimony contains two atoms.

The far greater difficulty lies in the determination of the way in which the atoms are arranged in the unit. These data are sufficient, but the interpretation is hard. To understand how it is attempted, and in some cases achieved, is best explained by models.

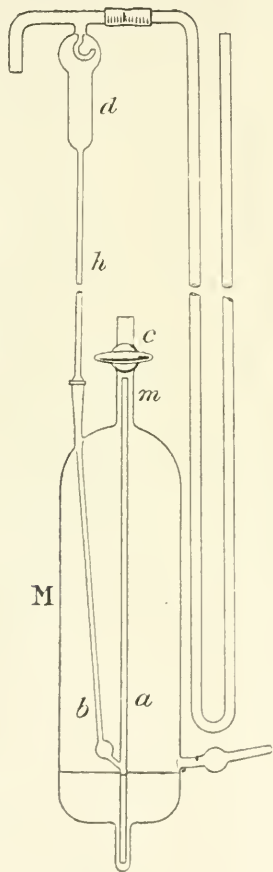
South African Association for the Advancement of Science.—(Honorary President, His Majesty the King).—The Fourteenth Annual Session of the Association will be held at Maritzburg, from Monday, July 3, to Saturday, July 8, 1916, inclusive, under the Presidency of Prof. L. Crawford, M.A., D.Sc., F.R.S.E.

A NEW SAFETY VALVE.

By M. S. LOSANITCH.

AMONG various safety valves for preventing the back-flow of water of water-pumps which have been tried in my laboratory it has been found that the form described below answers very satisfactorily the purpose for which it is intended.

It consists of a cylindrical vessel, *M*, provided with a nozzle connected by an indiarubber tube to the pump, and a glass tap, *c*, to let in air when required. In its interior is enclosed a T-tube of small internal diameter (not exceeding 2.5 mm.), its arm *a* reaching close to the tap *c*; the arm *b* is fused through the mantle as shown in the drawing, and connected by means of a joint with the tube *h*, so that the total length is about 80 cm. The top



of the tube *h* is widened and serves as a safety tube, *d*, and it is connected on one side to the vessel to be evacuated. It is advantageous to mount this apparatus on a wooden board and to fit a Bunsen manometer as indicated.

Before using this safety valve it is necessary to fill up the cylindrical vessel with mercury till its meniscus reaches in the interior of the T-tube the lower edge of the arm *b*. When the whole apparatus is pumped out and a back-flow of water occurs, the water fills the reservoir *M*. In order to prevent too strong a rush of water it is advisable to insert in the tube leading to the pump a glass tap whose stopper has a bore of 1 mm. approximately. The increasing pressure of the water column above the mercury forces up its level in the T-tube, closes both its arms, and shuts off completely the evacuated vessel from the

reservoir. If the cylindrical vessel has been charged with the proper amount of mercury this will happen when the water column has accumulated to a depth at most of 4 to 5 cm. above the mercury. The intruding water compresses the rarefied air contained in the reservoir almost to the atmospheric pressure, and if the dimensions of the apparatus are correctly chosen this will occur before the water reaches the top of the tube *a*.

(If the initial and the atmospheric pressure are designated by *P* and *p*, and the final volume of the compressed air, consisting of the volume of the arm *a* and the space beyond the mark *m*, is designated by *v*, then the volume of the reservoir at the moment when it is shut off is $V = \frac{vp}{P}$.)

In order to keep the apparatus within reasonable dimension *v* should be as small as practically possible).

As the pressure increases in the reservoir the column rises in the tube *h*, and when it has reached its maximum the tap *c* is carefully opened (the column will rise a little further) in order to allow the water contained in the reservoir to flow away through the water-pump. After turning off the tap *c* the reservoir is again evacuated, the mercury column falls, and the communication between the pump and the vessel to be evacuated is again automatically established.

When the water has flowed away and its pressure over the mercury has decreased, the mercury column breaks at the base of the T-tube; it often vibrates slightly, and if some of the mercury column should escape at this point the shortened column can no longer balance the atmospheric pressure, and it is vigorously driven into the safety tube *d*, which is provided with a hooked nozzle to prevent the mercury from being drawn right through it. In order to avoid the undesirable effect of this vibration the arm *b* is widened into a small bulb containing enough mercury to feed the column in case of emergency.

In order to ensure the efficiency of this apparatus it must be filled with the exact amount of mercury and always kept clean.

Chemical Institute of the
University of Belgrade.

NOTE ON THE RELATIONS BETWEEN THE CUTTING EFFICIENCIES OF TOOL STEELS AND THEIR BRINELL OR SCLEROSCOPE HARDNESSES.*

By J. O. ARNOLD, D.Met., F.R.S.,
Professor of Metallurgy in the University of Sheffield.

In papers recently read before the Iron and Steel Institute there has been a tendency to regard the Brinell and scleroscope numbers registered by hardened steels as an approximate measurement of their cutting efficiencies in the lathe. Indeed, it has been suggested that, instead of ascertaining the efficiency of high-speed steels directly in the lathe, the Brinell test might be substituted for the costly and prolonged proceeding of making systematic lathe tests. The purpose of this brief communication is to show that not only is there no relation between Brinell hardness and lathe efficiency, but also that a plain carbon turning tool with very high Brinell hardness may, on comparison with another tool of considerably lower Brinell hardness, register an efficiency of practically zero, whilst the tool of, say, 15 per cent lower Brinell hardness may run perfectly for, say, eighteen minutes, and during the last five minutes of the test cut cleanly at a blood-red heat before breaking down.

The Brinell hardness of a properly hardened tool is an almost negligible factor of efficiency. The efficiency depends almost entirely on the thermal stability of the simple or compound hardenites in the hardened steel. The

* Read before the Iron and Steel Institute, May, 5, 1916.

TABLE I.

University steel No.	Type of steel. Com- positions nearly identical for each type.	Duration of tests in minutes and seconds before breaking down.				Efficiency. Cubic inches of standard hard steel shalt removed.				Brine 1 hard- ness No. pres- sure, 3000 kilos. ; ball, 10 mm. diam.	Scleroscope hard- ness No. Average of four tests.
		1st grind.	2nd grind.	3rd grind.	Mean.	1st grind.	2nd grind.	3rd grind.	Mean.		
1523	Tungsten-chromium	10 7	11 45	9 26	10 26	47.4	56.3	43.3	49.0	600	82.8
1527	"	11 25	12 35	10 32	11 32	54.7	61.4	49.4	55.2	629 (b)	80.5
1533	"	10 26	11 50	11 31	11 18	48.9	56.7	55.0	53.5	578	80.3
1522	Tungsten-chromium - vanadium	14 17	17 59	13 40	15 19 (c)	72.3	96.2	68.0	78.9	600	80.3
1524	"	17 2	17 49	16 57	17 24 (c)	91.0	95.2	89.1	91.8	600	75.5
1528	"	16 2	17 52	16 57	17 24 (c)	84.1	95.7	89.1	89.6	600	76.3
1534	"	15 21	17 10	15 45	16 27 (c)	79.0	91.6	81.1	83.9	600	81.0

(NOTE.—The Brinell and scleroscope hardnesses were taken as near as possible to the hardened cutting edges of the various tools).

(a) It will be seen that with both types of steel the maximum efficiency is obtained on the second grindings of all seven tools.

(b) Duplicate test 629.

(c) Throughout these tests the cutting edge of the tool was red-hot at the breakdown points, and, indeed, for about five minutes previous to breaking down.

simple hardenite of plain carbon steel has a thermal stability of which the limit is certainly less than 300° C., whilst the compound hardenite of a C-W-Cr-V high-speed steel, also secured by water quenching, may be rendered stable up to a temperature of about 700° C. The proof of the foregoing enunciation is embodied in Table I.

If tested, *ceteris paribus*, with the steels in Table I., a hardened best crucible-cast plain carbon steel, containing about 1.25 per cent combined carbon, would endure for perhaps two seconds. Therefore its endurance would be roughly 0.3 per cent that of the W-Cr steels and about 0.2 per cent that of the W-Cr-V steels. Nevertheless, its Brinell hardness would be about 700 as against the 600 numeral registered by the high-speed steels. Again, according to the mean Brinell test (602) the W-Cr steels should average an efficiency of 0.3 per cent greater than the constant numeral (600) of the W-Cr-V steels, yet the actual efficiency of the latter is 63 per cent greater than that of the former. In a word, the Brinell and scleroscope tests, whilst valuable means of rapidly approximately determining the elasticity of structural steels, are valueless, or indeed worse than valueless, for estimating the varying thermal stabilities of the hardenites which mainly determine lathe efficiency.

The author and Prof. A. A. Read, D.Met., have shown (*Proc. Inst. Mech. Eng.*, Nov., 1915, p. 645) that there are four single hardenites; *i.e.*, solid saturated solutions of carbides, namely, iron hardenite ($\text{Fe}_{21}\text{Fe}_3\text{C}$), vanadium hardenite ($\text{Fe}_{22}\text{V}_4\text{C}_3$), tungsten hardenite (Fe_{26}WC), and ferro-molybdenum hardenite ($\text{Fe}_{24}\text{Fe}_3\text{Mo}_3\text{C}$), (this substance might be accurately classed as a sort of double hardenite). The double, triple, and possibly quadruple hardenites of high-speed steels yet remain to be discovered, but owing to a grant-in-aid of £200 from Sir Robert Hadfield, the author and Prof. A. A. Read, D.Met., of the University of Wales, are now proceeding with this complex research.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 8th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Lady Margaret Boscawen, Mr. A. F. Lake, Mrs. E. M. Neal, and Lady Petre were elected Members. The Secretary announced that His Grace the President had nominated the following gentlemen as Vice-Presidents for the ensuing year:—Sir Thomas Barlow, Bart., Sir William Phipson Beale, Bart., Charles Hawksley, Esq., The Hon. Richard Clere Parsons, Sir James Reid, Bart., The Right Hon. Lord Wrenbury, Sir James Crichton-Browne (Treasurer), and Colonel Edmond H. Hills (Secretary).

EXPERIMENTS ON THE NATURE OF THE PHOTOGENIC SUBSTANCE IN THE FIREFLY.

By E. NEWTON HARVEY.

PREVIOUS research on the subject of biophotogenesis has shown that at least three factors are necessary for the production of light, namely, water, oxygen, and a photogenic substance. A fourth factor is probably also involved, an oxidising enzyme, as in other organic oxidations. Concerning this enzyme nothing is known, at least nothing definite in the case of the firefly. Indeed, Kastle's observations indicate that in the firefly no direct oxidising enzyme (oxygenase) but only small amounts of an indirect oxidising enzyme (peroxidase) and a catalase are present (Hygienic Lab., Washington, D.C., *Bull.* 59, 1910, 92).

The old observation that many luminous tissues can be dried and ground up and will phosphoresce, when water containing oxygen is again added, gives us a simple chemical method of investigating the nature of the photogenic material. The dried material may be extracted with water-free solvents (since the photogen does not oxidise in absence of water), and extracted material as well as the residue from evaporation of the filtrate tested for phosphorescence by adding water. Or the dried material may be extracted with oxygen-free aqueous solvents (since the photogen does not oxidise with light production in absence of oxygen), and filtrate and residue tested as before by admitting oxygen. The first method is satisfactory, and has indicated that a large number of fat solvents will extract nothing from the dried tissue and yet leave the photogenic material unharmed. Indeed, the material may be extracted with boiling ether for twenty-four hours without impairing its power to phosphoresce. Boiling alcohol does destroy the power to phosphoresce, and the nature of its action is discussed below. These results, as well as the previous results of McDermott (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 1791; *Smithsonian Report*, 1911, 345) and Dubois (*Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 1912, xix., 86), using fresh watery material, show conclusively that the photogenic substance is not a fat or fat-like body of any kind.

The second method—that of extraction with oxygen-free water solutions—is not satisfactory because the photogenic substance breaks up, or at least loses its power to phosphoresce, on standing in contact with water for any length of time *even if no oxygen is present*. Many attempts were made to extract the dried material with aqueous solvents, and filter the extract in absence of oxygen before it was recognised that such attempts were futile because of the instability of the photogenic substance in oxygen-free water.

My experiments were begun in the winter of 1913 on firefly material collected at Princeton, N.J., and dried over CaCl_2 in a vacuum. (See preliminary note, Harvey, *Science*, 1914, xl., 33). I am greatly indebted also to Mr. F. Alex. McDermott, of the Mellon Institute, University of Pittsburgh, for an additional supply of material with which the work was continued. Mr. McDermott has been making experiments along similar lines with a somewhat different apparatus, and his results are likewise published in the *Journal of the American Chemical Society* (*loc. cit.*). As luminous material may be found which does not disintegrate in water the apparatus used for oxygen-free extraction is described below.

The material to be extracted is placed in the vessel *c* (Fig. 1), provided with a ground-in stopper connected with

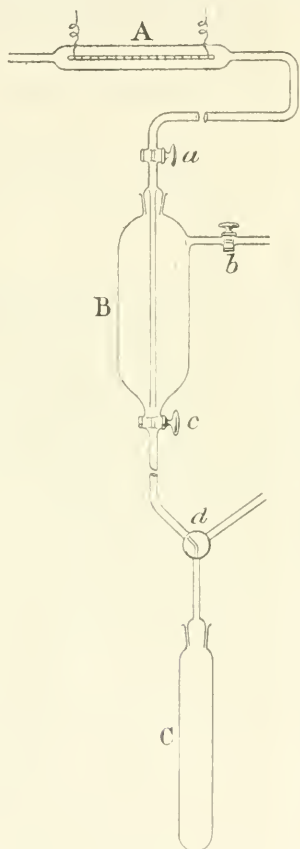


FIG. 1.

a 120° stopcock. The water to be rendered free of oxygen is placed in *B* after passing hydrogen through stopcock *c*, and closing it. *B* is connected through *A* with a hydrogen generator. The hydrogen is passed through potassium pyrogallol. By alternately exhausting *B* through *b*, connected to an air-pump, and refilling with hydrogen several times the water can be quickly rendered free of oxygen. *c* is then connected to *B* through *c*, and one of the arms of the 120° stopcock (*d*) whose other arm is connected with an air-pump. *c* and the arms of *d* are then exhausted. The 120° stopcock is then turned to connect *c* and *B*, and *c* is opened, allowing the pressure of the hydrogen to drive the solvent on the material in *c*. The proper amount of fluid

for extraction should be placed in *B* so that the hydrogen may follow it through and fill the chamber *c*. Then *d* is closed, when *c* can be disconnected and shaken during extraction. To filter the extract it is only necessary to connect one of the arms of *d* with a desiccator fitted with funnel and filter rack. When the desiccator is exhausted, *c* and the desiccator are connected, and the pressure of the hydrogen in *c* drives the extract on to the filter-paper. The firefly photogen begins to phosphoresce when the atmospheric pressure reaches 5 to 6 mm., which means an oxygen pressure of 1 to 1.2 mm. Consequently, it is necessary to use a good vacuum pump and make connections air-tight. I found that small bore lead tubing sealed with Khotinsky cement the best for the purpose.

If one extracts with distilled water for a short time (fifteen minutes) and then filters, on admitting oxygen the filtrate is found to be dark while the residue on the filter-paper shows the bright points of light characteristic of the power of the firefly. But if the extraction be carried out for an hour or more, neither the filtrate nor the residue will phosphoresce when oxygen is admitted. All of my experiments have been carried out in the dark, and the material observed at critical stages (as when the oxygen-free water was added) to make sure that no light appeared, and always with negative results. But to make sure that no very slow leakage of oxygen into the filtering chamber occurred, I have carried out the extraction in a special tube provided with a capillary sealed off during the extraction. After extracting in this tube for one and one-half hours and admitting oxygen no phosphorescence appeared. Thinking that possibly the photogen dissolved in the extracting fluid did phosphoresce, but only so faintly as to be invisible because distributed through a relatively large volume of extract fluid, the unfiltered extract was evaporated *in vacuo* to a small volume. This can be very easily done by placing the rubber tube from the vacuum pump over the capillary on to the special tube, exhausting, and then breaking the capillary through the walls of the rubber tube to connect with the air-pump. Even when concentrated, the extract gave no light on adding oxygen.

The photogen is therefore destroyed in distilled water without oxidation. The search for a watery solvent for photogen becomes then a search for a solvent in which the photogen is stable. The following solutions were tried in addition to distilled water. Extraction was allowed to proceed for from 1 to 1.5 hours.

1. Ringer's solution (as representing fairly accurately the concentration and composition of the firefly's blood).
2. 0.125 M NaCl.
3. Sea-water (a mixture of chlorides and sulphates of Na, K, Ca, and Mg).
4. 5 per cent NaCl.
5. 0.05 M NaOH and 0.01 M NaOH. The dried powdered firefly organs will phosphoresce strongly if sprinkled on the surface of 0.1 M NaOH.
6. 0.02 M HCl. Dried firefly powder will phosphoresce on 0.0125 M HCl and on 0.025 M HCl, but less brilliantly. Only one or two bright dots appear on 0.05 M HCl, and no phosphorescence occurs on 0.1 M HCl. If neutralised within two minutes after contact with the acid, the light does not appear in the 0.1 M HCl treated material nor become brighter in the 0.05 M and 0.025 M treated material.

In each case after extraction, oxygen was admitted and the solution shaken, yet in no case did light appear either in the undissolved residue or in the solution. The 0.02 M HCl extract was also neutralised as it is well known that the acid prevents biophotogenesis. The conditions of phosphorescence in the firefly are therefore more complex than at first supposed. Either the photogen, the enzymes, the enzyme activators, or all three, undergo changes which are not oxidative in nature, when the material stands in contact with water for a time sufficient to dissolve out the luminous material. Both McDermott's results and mine

agree perfectly, and while negative and disappointing they are deemed worthy of publication as indicating that water, oxygen, and a photogenic substance are not the only factors involved in light production, and also as showing the instability of the photogen.

My work with water-free solvents has been confined to those listed in Table I., which gives also the time of extraction, temperature, and results.

TABLE I.

Substance.	Temperature. Degrees.	Time. Hrs.	Extracted material.	Extract evaporated in vacuo.
Ether (cold)	20	72	+	—
Ether (hot)	35	24	+	—
Chloroform (cold) ..	20	72	+	—
Chloroform (hot) ..	61	8	+	—
Ethyl alcohol (cold) .	20	24	+	—
Ethyl alcohol (hot) ..	78.4	24	—	—
Ethyl alcohol and ether (equal parts) boiling	44	10	+	—
Carbon tetrachloride	20	48	+	—
Carbon disulphide ..	20	48	—	—
Acetone	20	48	+	—
Toluol	20	48	+	—
Amyl alcohol	20	48	Very faint(a)	—
Ethyl butyrate	20	48	Very faint(a)	—

(a) The material was washed with ether to remove the amyl alcohol and ethyl butyrate.

A plus sign indicates phosphorescence when water is added, and a minus sign indicates no phosphorescence. Both the original extracted material and the residue of the filtered extract evaporated to dryness were examined. The results indicate that the photogenic substance is not a fat or oil, and also not a lecithin. I am aware that the lecithins are difficult to extract *in toto* from the cell, but this can be accomplished by a mixture of hot ether and alcohol, and yet a mixture of hot ether and alcohol will extract nothing which will phosphoresce from the firefly powder. We may safely say that the photogen is not a lecithin.

Of all the solvents tried only hot alcohol and cold amyl alcohol and ethyl butyrate gave results that would indicate a possible solution of the photogenic substance. And yet there is nothing in the filtrate residue that will phosphoresce when water or a neutralised 3 per cent solution of H_2O_2 is added. Thinking that oxidising enzymes might be necessary, and that these had not been extracted by the fat solvents although the photogen had, the filtrate was also tested by adding a water extract of firefly organs, fresh or preserved with toluol or chloroform, and also by potato-juice which contains considerable quantities of oxidising enzymes. In no case was phosphorescence observed. The boiling ethyl alcohol (see Note), cold amyl alcohol, and ethyl butyrate must therefore break up the photogen. It is the alcohol itself and not the temperature (78.4°) of boiling alcohol which is responsible for the destruction of the photogen, as the dried powder will withstand this temperature for twenty-four hours without any appreciable diminution in its power to phosphoresce. McDermott finds that liquid sulphur dioxide and liquid ammonia also destroy the photogenic power.

(NOTE).—The 99.8 per cent absolute alcohol was distilled over metallic calcium and collected in a receiver protected from the air by $CaCl_2$ in order to remove the last traces of water).

The powder obtained by drying cultures of luminous bacteria behaves similarly to the firefly material.

These results indicate that it will be a vastly more difficult problem to isolate and identify the photogenic substance than might at first be supposed.—*Journal of the American Chemical Society*, xxxvii., No. 2.

MAGNESIUM.*

By W. M. GROSVENOR.

THE alkali earth division of the second group in the Periodic Table consists of more or less soft white metals and all show great avidity for oxygen, decomposing water more or less readily. None except aluminium has found large commercial use but of the others magnesium leads the list by a long distance. Its chief uses are:

1. Scavenging alloys, *i.e.*, clearing up oxides of other metals and making far denser, cleaner, stronger, and more homogeneous alloys. It is valuable in aluminium, nickel, copper, brass, bronze, &c., and special steels, because of its intense avidity for both oxygen and nitrogen.

2. Alloying itself, with aluminium or aluminium containing traces of one or more of the other metals Cu, Ni, Zn, Pb, Bi, Sb, Fe, &c. Magnesium greatly modifies crystallography and physical properties and alloys readily with most metals and melts at a convenient heat.

3. Illumination, as in military uses, for shrapnel trailers, star bombs, flare lights, &c., and in photography for flashlights. Its easy inflammability (about 800° C.), the high heat of combustion (134,000 cal.), the relatively low heat of vapourisation (1100° C.), the intensely white oxide produced, and the high temperature of volatilisation of this oxide, are the essential factors.

Market and Prices.

How much is used? Records of imports for the year prior to the war indicated 38,000 lbs. About 100 lbs. a day, therefore, seemed to be a safe production to undertake. Prices before the war had been very steady around 1.45 dols. per lb. but it seemed reasonably certain the cost need not exceed 1.00 dol. per lb., and after the war began the prices being paid for remnants of imported lots quickly rose to 2.50 dols. Some of the first demands here were from wholly unexpected quarters, in surprising amounts and at amazing prices. The most urgent, almost pitiful demands, came from quarters that were not even suspected to be interested in the least. One consumer has contracted for 24,000 lbs. and another 15,000, these two alone taking for strictly domestic use more than was supposed to be the total importation. There are at least three other buyers of similar quantities but exact amounts are not yet established. Sales are largely made by yearly contract and even at present prices the consumption for strictly domestic use is about 50 tons. We found that a great deal of the material was being imported under other names and most carefully disguised—secrecy being preferred to economy. Prices as high as 10.00 dols. per lb. were gladly paid at first for domestic product. For some months then the prices jumped around from 5.00 dols. to 7.50 dols. but every effort was made to reduce conditions to some sort of order by dealing direct with the consumer. This was partly the result of a deliberate policy for better and more intelligent service of the consumer's precise demands as to quality and delivery, but partly also the result of meeting quite unexpectedly the competition of our own product at prices from 25 per cent below to 50 per cent above the prices we had made. Some of the New York's clever War goods brokers added 10 per cent each through a chain of four or five middle men. Others assumed direct quotations to have already been through this process and knocked off 20 per cent, trusting that "real cash business" would squeeze down the middle men they supposed to exist and still leave 5 per cent for the real seller. Now, however, for a number of months the price has been practically fixed at 5.50 dols. per lb. of "Guaranteed 99 per cent," actually about 99.5 per cent. Occasionally a lot that has been picked up in the ante-

* Address before the New York Section of the American Electrochemical Society, in joint session with the New York Section of the American Chemical Society, Chemists' Club, February 11, 1916.—From the *Journal of Industrial and Engineering Chemistry*, viii., No. 3.

bellum market for speculation is let go at lower figures, or a lot of lower grade material comes on the market from abroad, but there is practically no volume of these sales.

In spite of the beautiful appearance of the German bars they rarely exceeded 98 and often fell as low as 96 per cent. The process of extrusion conceals impurities by drawing them out into minute threads. It is safe to say that the regular commercial grade of metal made here now is superior to anything ever imported.

Reasons for these Prices.

It may seem ridiculous to ask or pay such prices. Let us consider. The alloy market constitutes the bulk of the business and governs prices. In aluminium castings, for instance, less than 2 per cent of magnesium cleans up the aluminium and leaves $\frac{3}{4}$ to $1\frac{1}{2}$ per cent in the casting, about doubling its tensile strength and quadrupling its resistance to shock or jar. It reduces the cost of machining more than 50 per cent, halving the number of resets on the cutting tool, giving clean-cut machine surfaces, and permitting a polish to be secured with the last cut instead of a separate operation. With care, $1\frac{1}{2}$ per cent of magnesium at 5.50 dols. per lb. is all that is needed; i.e., $8\frac{1}{2}$ c. per lb. of casting actually required to do the same work. The increase in strength means, in some cases, a reduction in weight of casting of 50 per cent and generally not less than 25 per cent. The saving in machine work alone when the casting is to require much machine work more than pays for the use of magnesium.

So much for the consumer or user. Now, the manufacturer of magnesium has at present certain considerations (of necessity rather than mere excuse) for the high prices. Cost of production abroad prior to the war approximated 1.00 dol. per lb. Sales in England were about 1.30 dols. and here about 1.45 dols. per lb. At that time $MgCl_2 \cdot 6H_2O$ was selling for about 18 dols. per ton. Present prices here are now about 60 dols. Other chemicals used in the manufacture have increased to ten times their normal price. One other factor, i.e., insurance, must be considered in two forms:—First, the insurance against cut prices and dumping that may come immediately upon the close of the war, making the plant and market-development work absolutely worthless. Second, the insurance against partisan interference. As a matter of fact in the case of two plants not a pound of material from either of which has gone for foreign military purposes so far as we know, there have been repeated efforts at molestation and some serious interruptions.

In considering prices it is well to mention separately export prices. Before the war nearly all the magnesium for England, as well as the United States and France, came from Germany. Since the war both France and England are producing in considerable quantities of excellent purity. This fact and the failure abroad to realise the strenuous conditions here, account for the unwillingness of buyers abroad to pay more than 3.50 dols. for powdered metal (all the above-named prices were ingot or bar).

Present Production.

At present there is being produced here at two points about all the present alloy market will absorb, and an increase of plant is being made of about 25 per cent of the present capacity. One other producer makes only about his own requirements. Two others are soliciting business, but have failed to fill orders—in one case the order is not over a year old, and still stands unfilled. All told, we believe the present production is at the rate of something over 1,000,000 dols. a year, and will be slightly in excess of the present domestic needs.

Possibilities.

The use of the metal for scavenging purposes depends on price of metal compared with price of material to be scavenged. For use with copper, brass, bronze, &c., the magnesium can be used at far higher prices than for steel

But the big consumption of the material can come only when it directly replaces aluminium as the predominant metal in the alloy and arrives at a correspondingly low price. It makes beautiful castings, machines easily and well, is about a third lighter than aluminium, and can be made about two to four times as strong. The coefficient of expansion reported is practically the same as for aluminium. When properly pure (over 99.5 per cent) it is apparently quite as resistant to corrosion as aluminium, equal if not superior in electrical conductivity (about half that of copper), and superior in heat conductivity to aluminium (also about half that of copper).

Processes.

I. *Reduction of Fused $MgCl_2$ with Sodium* involves the production of metallic sodium; we have been using the Castner process for this purpose to satisfy ourselves just what the sodium would cost and what the possibilities in this direction were. Existing conditions, the demand for sodium and sodium peroxide, forbid its consideration with a minimum of about 2 lbs. of sodium consumed for every pound of magnesium produced, and the necessity of producing dehydrated fused $MgCl_2$ to start with.

II. *Electrolysis of the Fused Double Chloride* (usually $MgCl_2 \cdot 2KCl$) has been perfected, and is very largely used abroad. We have commercially used and studied the process here, and, with the cheapest water-power and chloride, prices even under normal conditions by this process must rule above 1.00 dol.

III. *Reduction with Carbon* (patented) is absolutely fascinating in its possibilities. The product is a black or grey powder. Believing such a product would be valuable, the manufacture was carried out on a scale of about 25 lbs. per hour. As the difficulty of selling the product became apparent, much time and effort were devoted to attempts to recover the metal in fairly pure form. Owing to serious objection both on the side of cost and regularity of product this process was superseded.

The other processes—electrolysis of dissolved MgO (patent applied for), reduction of fused $MgCl_2$ with aluminium (patent applied for), reduction of oxide or carbonate to slag-forming residues (patent applied for), &c.—will be discussed on some other occasion when the engineering problems they involve are believed to be finally solved in the best way and the Patent Office has finished considering them. The chemical side of each has been thoroughly worked out, however, so that some conclusions may be drawn from the large laboratory or small commercial operations. These may be of considerable interest.

At least one of the processes appears to be adapted to produce directly metal averaging 99.6 per cent purity in tons per day instead of pounds. Laboratory tests give a raw material cost of 4 c. per lb. of magnesium and indicate a fuel cost which approaches 3 c. as a theoretical limit, though the practical figure will probably be several times as high. The final selection of various possible engineering means and methods remains to be worked out, but it scarcely seems possible that either labour or repairs should succeed 2 c. per lb. Thus if commercial yields maintain the experimental level and three times the theoretical power is commercially required, we have prospects of a net factory operation cost (without interest, amortisation, insurance, patent, administration, or selling) of 17 c. per lb. If only 75 per cent yield is obtained this net factory cost would be about 22 c., or a total cost with all overhead expenses of 35 c. and a selling price of 40 c. to 50 c. according to tonnage.

It may be asked with perfect propriety:—"Why talk about it now? Some fool will certainly want you to make a contract with him at lower prices, possibly at 50 c. He will not realise that it is only the present price of 5.50 dols. that justifies or even make possible the 1000 dols. and 10,000 dols. experiments that have been tried and must be tried again, and perhaps again, during the next three to five years before the tide turns. You will be pestered for years

with this 17 c. talk." We have carefully considered this probability. The men who are doing this work do not cultivate talkativeness as a preference. Just at this time, however, certain consideration of public welfare should take precedence of preference. National self-preservation demands the subordination of personal interest. If we expect representatives at Washington to jettison the pork barrel, the army post, the high-tide navy yard, and political trading generally, and give us a fighting chance for our lives in the scrap that is certainly coming, we must set the example of considering national interest first. If we are to have the army and navy preparedness for which we have already wasted more money than Germany has paid for her wonderfully efficient fighting machine, if we are to have any preparedness instead of repairs or regrets, we must co-operate with all we have in service, information, and suggestion.

Therefore, at the risk of criticism and possible financial sacrifice it seems to be a duty at this time to point out what may possibly be expected of magnesium. Few realise the extent to which it is valuable in military work. One of the great foreign explosive experts stated that he would be glad to pay 1.50 dol. per lb. for 500 tons. A single contract for shrapnel being executed in this country would require about 50 tons. The illuminating bombs to make daylight over the enemies' works and trenches consume large quantities. The trailers attached to shells serve at night to show the effectiveness of the fire. For all these purposes magnesium produces a result that cannot be approached by antimony or aluminium. But consider what it means to aeroplane, dirigible, and motor construction, to high-speed engines of every type, to reduce weight one-third and double strength. This material has a density of 1.75, and may be hot-rolled to a tensile strength of 35,000 lbs. per square inch, or cold-rolled very much higher. Although five or six men are being kept practically all their time on the development of these possibilities, the broad quick development is a task for the energy of hundreds, even thousands. Feeling the responsibility which knowledge of the possibilities entails, it became the duty of those in charge of this work to let others know and be active in their side of the preparation—the application of the material.

THE EXTRACTION AND SEPARATION OF THE RADIO-ACTIVE CONSTITUENTS OF CARNOTITE.*

By H. M. PLUM.

(Continued from p. 211).

SINCE no single method has yet been found that is applicable for treating all carnotites it was thought desirable in this work to make a study of some of the principal methods already proposed, and to determine therefore to what extent these methods must be modified in order to be most effective in the treatment of our ore. Accordingly the following experiments were made:—

(a) *Extraction of Vanadium with Caustic Soda.*—This method is based on the fact that a vanadium ore forms a soluble metavanadate by treating it with a caustic soda solution. Fischer, in a paper on the extraction of vanadiferous sandstone concentrates (*Met. Chem. Eng.*, 1912, x., 469), states that in his opinion only methods which employ a caustic alkali promise commercial success. In working on crude ore Fischer found it impossible by wet methods, even by boiling, to obtain satisfactory results unless he used commercially prohibitive quantities of alkali, in which case nearly complete extraction of vanadium was obtained. Excessive consumption of caustic alkali was apparently due to its action on the silica in the ore. With carnotite, however, he was able

to get from 87 to 98 per cent extractions of vanadium with much smaller consumption of alkali by treating them in the following manner:—The concentrates were added to water containing alkali in the proportion of five parts of concentrates to one part of alkali, and the whole mixed to a pasty consistency and then evaporated to dryness, finishing at a temperature ranging between 200° and 300°. This method when applied to a crude ore, on the contrary, yielded only about a 65 per cent extraction of the vanadium.

The following are the results of my experiments:—100 grms. of carnotite were mixed with 50 grms. of caustic soda dissolved in 200 cc. of water and boiled for three hours in a flask with a reflux condenser. A sample of the solution then showed about 45 per cent of the vanadium had been extracted. When the mass was boiled for six hours longer the amount of vanadium extracted had not increased. Thus it was evident that this method could not be used if the vanadium were to be removed completely by a single treatment. Fusion with caustic soda was tried, but not very thoroughly investigated, for it was evident that with such a procedure much difficulty in filtering and washing would be experienced, because some of the silica in the ore was converted into sodium silicate, which on acidifying interfered with subsequent processes.

(b) *Treatment of Carnotite with Carbonate of Soda.*—A method of extracting uranium and vanadium from carnotite with sodium carbonate solutions has been patented by Haynes and Engler (U.S. patent No. 808,839, 1905). This method, as described by Moore and Kithil (*Bulletin* 70, 1913, Bureau of Mines), involves the boiling of the carnotite ore, which has been crushed to twelve mesh with an alkaline carbonate solution until the uranium and vanadium have dissolved. The time of boiling and the strength of solution depend upon the proportion of the two elements present. In the clear filtrate resulting the uranium is then separated from the vanadium by precipitating the former with sodium hydroxide. This process in actual operation with carnotite is said to give an extraction of 80 per cent of uranium and 60 to 65 per cent of vanadium.

After some preliminary experiments, which seemed to promise good results, the above method with modifications was carefully investigated. 100 grms. of carnotite were boiled with reflux condenser for three hours with 100 grms. of anhydrous carbonate of soda dissolved in 250 cc. of water. After filtering, a sample of the filtrate was neutralised with acid, reduced with zinc and sulphuric acid, and the resulting solution titrated with potassium permanganate. The solution was filtered and the residue treated twice successively in a similar manner with soda solutions, except that the heating in each of these last two cases was continued for only 1½ hours. Analyses of the solutions showed the relative extracts to be approximately as 9 : 2 : 1/3. A test on the third filtrate showed very little uranium present. When these three solutions were combined and concentrated by boiling a yellow precipitate appeared, which was found on subsequent analysis to be sodium uranyl carbonate. By removing this precipitate and further concentrating the filtrate it was possible on cooling to low temperatures to crystallise out a large part of the unused sodium carbonate in a form easy to wash free from impurities. When the insoluble residue free from the three consecutive treatments with soda solutions was boiled with hydrochloric acid the filtrate was green in colour and contained large quantities of vanadium. This experiment showed that two treatments with a boiling sodium carbonate solution removed most of the uranium from the ore, giving a solution from which both the uranium and most of the soda could be recovered by simple processes. This method, however, had failed to bring the vanadium completely into solution, a result which is in accord with that found by Haynes and Engler, as cited above.

(c) *Treatment of Carnotite with Carbonate of Soda in the Presence of an Oxidising Agent.*—Since the treatment

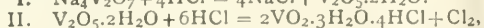
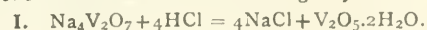
* *Journal of the American Chemical Society*, xxvii., No. 8.

of carnotite with soda alone, as described in (b), had failed to bring all the vanadium into solution, it was thought that by converting this element into its most highly oxidised form its extraction might be more complete. In impure carnotites, in which the vanadium often occurs both in the trivalent and pentavalent forms, it has been observed that the vanadium dissolves much more readily in alkaline solvents in the latter condition. With these facts in mind, therefore, the following experiment was made:—

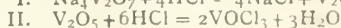
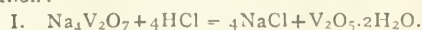
100 grms. of carnotite were boiled with reflux condenser for forty-one hours with a concentrated sodium carbonate solution. The heating was continued for so long a time in order to secure maximum extraction by the soda alone. Samples of the solution were examined from day to day, as in (b), but no increase in extraction was noticeable after the boiling had continued twenty-six hours. During the last six hours of the boiling a current of chlorine gas was passed into the solution, but on comparing samples of the solution both before and after the introduction of the chlorine gas no change in the vanadium content was found. In this experiment nearly all of the uranium was found in the soda solution, while a considerable part of the vanadium was left in the insoluble residue. These facts show that that part of the vanadium not readily soluble in a soda solution is present in some inert form—probably a silicate, such as roscoelite.

(d) *Treatment of Carnotite with Hydrochloric Acid.*—Among the various methods of treating carnotite is one proposed by Moore and Kithil (*Bulletin* 70, 1913, Bureau of Mines), which consists in treating the ore directly with concentrated nitric or hydrochloric acid. Pure carnotite dissolves in cold, even dilute acids. In the case of vanadiferous silicates, such as roscoelite, Moore and Kithil state that they were able to decompose such ores by boiling them for an hour with the concentrated acids. With the ore used in this work hydrochloric acid did not seem to bring the vanadium completely into solution, for in an experiment in which 5 grms. of the ore were boiled with concentrated acid for intervals of twenty to thirty minutes, ten or twelve successive treatments were required to extract all vanadium. In dealing with kilogram lots, where the ore had been previously treated with sodium carbonate solution, the residue, after three consecutive treatments with concentrated hydrochloric acid diluted with three times its volume of water and boiling for two or three hours, still held vanadium. Although Moore and Kithil are correct in stating that pure carnotite is readily soluble in hydrochloric acid, the facts just stated show that so-called carnotite of the kind here studied—the one which constitutes the bulk of the material available in America for technical processes—is a complex mixture, not all of which is readily attacked even by boiling hydrochloric acid.

(e) *Treatment of Carnotite with Dry Hydrogen Chloride.*—It was shown by Smith and Hibbs (*Journ. Am. Chem. Soc.*, 1894, xvi., 578) that sodium pyrovanadate is acted on by dry hydrogen chloride between room temperature and 440° with the formation of common salt and the complete elimination of the vanadium in volatile form. The application of a gentle heat caused a reddish brown vapour to appear, which condensed in the combustion tube as an oily liquid easily taken up by water. They explained the reaction in this case in the following way:—



except that they were not certain that the volatile compound had the composition $2\text{VO}_2 \cdot 3\text{H}_2\text{O} \cdot 4\text{HCl}$. Ephraim (*Z. Anorg. Chem.*, 1903, xxxv., 66), however, in working on the same problem showed that the volatile compound of Smith and Hibbs is vanadyl trichloride, VOCl_3 , and has given the following equations in support of his concentration:—



In analysing carnotite Hillebrand (*Am. Journ. Sci.*, 1900, x., 120) has used this method for the separation of vanadium. It was necessary, however, for him to oxidise with nitric acid any vanadium reduced during the process, and to repeat therefore the treatment with dry hydrochloric acid gas before complete separation could be effected.

To see if this same method would remove the vanadium from our ore the following experiments were made:—20 grms. of carnotite were heated for one or two hours in a retort through which dry hydrogen chloride was passed. Reddish brown fumes of vanadyl trichloride appeared at once and condensed in the neck of the retort or collected in the water in the receiver. During the process the retort was frequently shaken so as to ensure contact of the gas with all parts of the ore. Seemingly the method promised success, but analysis of the distillate showed that only about 20 per cent of the vanadium had been removed. On continuing the process for some time longer with increased heating more of the vanadium passed over, but the distillate at these higher temperatures contained considerable ferric chloride. When the involatile residue was washed with water and the filtrate treated with sodium hydroxide a heavy precipitate of sodium uranate formed, indicating that during the operation the uranium had been brought into a condition soluble in water. On account of the appearance of the iron in the distillate and the low percentage of vanadium extracted the process was modified as follows:—An electric furnace was substituted for the retort in order to be able to control the temperature. 10 grms. of the dried ore were placed in a quartz tube into which dry hydrogen chloride gas was passed as the temperature was gradually increased. This tube was frequently rolled to ensure uniform heating and mixing, and the process continued for the greater part of a day. In the light of Hillebrand's (*Am. Journ. Sci.*, 1900, x., 120) observations—i.e., that hydrochloric acid reduces a good deal of the vanadium and leaves it in a condition incapable of forming the volatile body—some dry chlorine gas was conducted through the tube during the latter part of the period in the hope that the vanadium would be kept completely oxidised and consequently a complete extraction be obtained. On examining the distillate, however, it was found that ferric chloride had again been carried over and that not more than about 40 per cent of the vanadium had been removed from the ore, even when the process had been continued throughout the day. On account of the slowness of the reaction and the incompleteness of the extraction the method was abandoned as an impractical one for treating carnotite on a large scale. It is probable that all the vanadium in the form of true carnotite is volatile under the conditions of the experiment, incomplete extraction being due, as in other methods, to the presence of vanadium silicates.

(f) *Treatment of Carnotite with Nitric Acid.*—In working on the new American ore, to which they gave the name carnotite, Friedel and Cumenge (*CHEMICAL NEWS*, 1899, lxxx., 16; *Comptes Rendus*, 1899, cxxviii., 532), after having extracted the vanadium by using dilute nitric acid, were able to separate the vanadium in the filtrate from other ingredients by evaporating the solution to dryness. Under these conditions they claim that vanadium, in excess of nitric acid, becomes insoluble upon evaporation and can be separated quantitatively from uranium, whose nitrate is soluble in water. Hillebrand (*Am. Journ. Sci.*, 1900, x., 120), however, in using this method of Friedel and Cumenge on some complex ores, found that he could not always get perfect separation, because it was impossible for him, first, to prevent a little of the vanadium going into solution with the uranium, and second, to prevent small amounts of the uranium being retained with the vanadium.

In working on our carnotite it was not possible with dilute nitric acid to get the vanadium completely into solution, as had Friedel and Cumenge. Besides, when the filtrate obtained in this way was concentrated the insoluble

vanadium precipitate which formed carried with it radioactive matter. These results indicate that nitric acid is not a suitable reagent for the primary treatment of carnotite. Naturally there are other reasons why the use of nitric acid would be avoided if possible in a technical process.

(g) *Treatment of Carnotite with Sulphuric Acid.*—A method of treating carnotite, originated by Herman Fleck, which uses dilute sulphuric acid directly on the crushed ore, is said to have been employed practically for extracting uranium and vanadium from carnotite. This method, which brings the two elements mentioned into solution, leaves the radium in the residue.

With our ore that part of the vanadium held in the residue left from a carbonate treatment, such as described in (c), could be removed if treated with sulphuric acid. In an experiment on 100 grms. of material this extraction was practically complete when the residue mixed with 35 cc. of concentrated acid and 115 cc. of water was heated to boiling for two and a-half hours. The extraction of vanadium was very complete when the ore, mixed with sulphuric acid and water, was heated until the excess of acid slowly fumed away. This method, nevertheless, even though it did remove uranium and vanadium completely, was not used because of the difficulties it involved in recovering radium with any high degree of efficiency.

(h) *Treatment of Carnotite with an Acid in the Presence of a Reducing Agent.*—In all the acid extractions, except perhaps in some stages in the nitric acid treatment, the filtrate appeared green or blue, depending upon the degree to which the vanadium had been reduced. Acid solutions of vanadium pentoxide are reduced to vanadium dioxide in the presence of sulphurous acid and by the evaporation with hydrochloric acid. Magnesium with hydrochloric acid reduces the pentoxide to vanadium trioxide, while zinc and hydrochloric acid carry the reduction to vanadium monoxide. Since vanadium, therefore, takes a reduced form in acid solutions it was thought that the introduction of a reducing agent at the time the acid was acting on the original ore might perhaps increase the degree of extraction. Accordingly 5 grms. of ore were placed in each of two flasks containing 3 cc. of concentrated sulphuric acid diluted with 15 cc. of water. In the one flask were added some pieces of zinc and the two solutions heated to boiling for some time under the same conditions, but when the filtrate was examined no increased extraction had occurred from the use of the reducing agent. Similar experiments, using dilute sulphuric acid with and without the addition of sulphur dioxide, showed no difference in the degree of extraction.

As a result of the foregoing experiments it was evident that this carnotite held part of the vanadium in a condition very difficult to remove by a single operation. In studying some of the Colorado carnotites Hillebrand (*Am. Journ. Sci.*, 1900, x., 120) had found the vanadium to exist in the ores in two distinct forms: (a) the pentavalent vanadium, quite easily soluble, and (b) the other a trivalent form, a vanadiferous silicate, extremely difficult to bring into solution. While pure carnotite dissolves at once in cold dilute nitric acid the vanadiferous silicate yields only to more powerful attacks. The ore used in this work resembled the latter closely in its characteristics, and after the series of preliminary experiments it was decided that it would be more advantageous not to try to remove the vanadium by a single process, but to treat the ore by methods calculated to recover the radio-active materials, leaving the vanadium to be dealt with wherever it occurred in the various solutions. On the basis of the foregoing work and that described in succeeding pages the following method was adopted as the most satisfactory:—The ore was treated first with a boiling solution of sodium carbonate, then with hydrochloric and nitric acids respectively, and finally with sulphuric acid. The details of the complete process, with descriptions and discussions of how the different radio-active ingredients were obtained, are given below.

(To be continued)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

PRESIDENTIAL ADDRESS, BY DR. ALEXANDER SCOTT,
F.R.S.*

It is exactly seventy-five years to-day since the Chemical Society of London met for the first time in the rooms of the Royal Society of Arts, after a preliminary meeting on February 23, 1841, had decided "*That it is expedient that a Chemical Society be formed.*"

At this first meeting the names of those who had consented to become original members of the Society were read, and two more were added before the first list was printed in the first number of the *Proceedings*, being seventy-seven in all.

Since that date the Society has met regularly on or about March 30 under a great variety of conditions, but never, with the exception of last year, in circumstances at all approaching those at present prevailing throughout Europe and over the entire globe.

The Crimean War in 1854 to 1856 is not even mentioned in the Reports of the Council or in the Presidential Addresses for these years, nor in still more recent times is the Boer War of 1899 to 1902 even referred to. These wars do not seem in any way to have awakened in our rulers any appreciation of the increasing part chemical science was destined to play in all warfare in the future.

On the other hand, the increased possibilities for the destruction of human life on a greatly magnified scale by the application of scientific methods had tended to make civilised nations regard war as well-nigh impossible. Most of us, I think, had ceased to believe that such a war as the present, with its absolutely reckless employment of human life as mere *Kanonen Futter*, to use the barbaric but expressive nomenclature of our enemy, could occur amongst so-called civilised peoples, and, short of demonstration, we could never have believed that our own science could have been so utilised and prostituted for the furtherance of its unscrupulous aims by any cultured nation.

In the earlier years of the Society's life it seems to have been sufficient for the President to read the Report of the Council at the anniversary meeting, and sometimes the Report and the Balance Sheet, together with the appropriate headings, were contained on two pages of the *Journal*. Succeeding years have added considerably to what has been expected from the occupant of this Chair, and now at each anniversary meeting he is expected to deliver a formal address on some subject closely connected with the life of the Society as "*a body politic and corporate,*" or on some subject of more purely scientific interest.

To-day, our seventy-fifth anniversary, suggests that the former of these subjects may fittingly form the theme of my remarks to you. Many thoughts arise in our minds on such an occasion, and lead us to reflect on the state of chemical science before the Society was founded, as to the aims and purposes for which it was deemed "*that it was expedient that a Chemical Society be formed,*" and to examine the measure of success which has been achieved by the Society in fulfilling the objects of its founders, investigating any failures in the carrying out of these aims, and devising methods whereby its usefulness may be increased either along the old or along new and more effective lines. To assist us in this, a brief history of our Society and of its aims as set forth by many of my illustrious predecessors at various times and in divers manners may be useful at the present time when so many changes are in the air and when the British public seems at last to be awaking to the important role modern science, and especially our own department of it, plays, and must continue to play, in every branch of domestic, commercial,

* Delivered at the Ordinary Scientific Meeting, April 6, 1916.

and national life. Therefore I venture to place before you these jottings from our life-history in the spirit expressed in the quaint words of the famous author of "The Sceptical Chymist": "Partly because I am not unapt to think that they may come abroad seasonably enough, though not for their author's reputation, yet for other reasons."

One of the letters received at the foundation of the Society was from Henry Fox Talbot, one of the pioneers in photography, in which he expressed the view that the science of chemistry alone was not sufficient to engage a society, and suggested a joint society for chemistry and electricity. How erroneous this view was is shown by the history of our own and similar societies.

The Chemical Society of London, as it was called when founded, is the oldest existing society devoted to the furtherance of chemistry, but within a month of its foundation the Pharmaceutical Society was formed, to be followed later on by the Chemical Society of Paris in 1858 and of Berlin in 1867, and by the American Chemical Society in 1876. Even at home, so vast has the field of chemical activity become, that we have had to detach vigorous and flourishing offshoots from our own body, which, whilst working in perfect harmony with the parent society and containing many members of it, devote themselves to special branches. Of these I need only mention the Society of Public Analysts (1874), the Institute of Chemistry (1877), and the Society of Chemical Industry (1881).

Looking back to the times of the "father of chemistry and the brother of the Earl of Cork" (although I always have regarded him as the grandfather rather than the father of our science) we wonder whether much progress has been made when we read in the "Introduction to the Sceptical Chymist," from which I have already quoted, "That of late chymistry begins, as indeed it deserves, to be cultivated by learned men, who before despised it, and to be pretended to by many, who never cultivated it, that they may not be thought to be ignorant of it." A perusal of our Parliamentary and legal reports leads us to wonder how our legislators ought to be classed in accordance with the above statement, and to doubt whether the attitude of so-called learned men had done much more than "begin to change" during these two centuries.

It is not altogether without significance that the beginnings of this change, the foundation of the Royal Society and of the real initiation of the experimental method into true science by Robert Boyle and his contemporaries, followed closely on the Civil War, and at a time when thoughtful men were striving once more to direct the energies of the country into peaceful and useful lines after the convulsions produced by military strife.

From the time of Boyle onwards for another hundred years or so the gradual substitution of careful experimental work in place of metaphysical speculations on the reasons for chemical and physical phenomena added much to the store of real knowledge. The rise and development of the phlogistic theory, the ingenuity of the theorems by which it was supported, and its final overthrow by the logical and brilliant experimental work of Lavoisier, illustrate this phase of the progress of scientific method.

My patriotic and perhaps grasping nature tempts me oftentimes to think that, without unduly sacrificing truth, the famous claim of Wurtz that "chemistry is a French science founded by Lavoisier of immortal memory," might be paraphrased by changing "French" into "Scottish" and substituting "Black" for "Lavoisier." There can be but little doubt that the great progress in chemistry dates from the experimental research of Joseph Black in 1775 on "magnesia alba" and his introduction of the chemical balance as the supreme arbiter on matters of chemical change. Chemistry then became an exact and quantitative science, and by means of the balance all changes and reactions and the rearrangements of matter could be traced with certainty, new elements and new compounds discovered, and new laws of nature revealed.

Lord Brougham, who attended Black's lectures, in his "Philosophers of the Time of George III." claims that "the physical sciences have few more illustrious names to boast than that of Joseph Black." He had "the good fortune of opening to mankind new paths in which both himself and his followers successfully trod, enlarging to an incalculable extent the bounds of human knowledge." This was due to "the happy union of strong but disciplined imagination with powers of close undivided attention and ample resources of reasoning which forms original genius in scientific pursuits." "His modesty in publishing his speculations and his genuine devotion to the investigation of truth for its own sake led to his incontestable claim to be regarded as the founder of modern chemistry being oftentimes overlooked."

Black was one of the earlier members of a galaxy of brilliant investigators who flourished from about 1750 through the turmoils of the time of the French Revolution and the European wars which culminated in Waterloo. In those war-stricken times, as at present, although to a much more limited extent, the vital importance of chemistry to the national life, and even to its very existence, was plainly demonstrated, but, as now, was recognised much more clearly by our adversaries than by ourselves. Witness the invention of the Le Blanc soda process in France, which was destined, however, to do more for us than for anyone else, leading to an enormous increase in our chemical manufactures and trade, extending with its ramifications to the present day as the "heavy chemical trade." The beet-sugar industry and the methodical production of nitrates further indicate how clearly Napoleon grasped the situation and strove to render France independent of England and her colonies.

A century ago chemists in this country were vigorously at work, and epoch-making discoveries both in theory and in practice were the natural outcome. The atomic theory of Dalton, the isolation of potassium and sodium by Davy, and his proof that chlorine was an element, date from the early years of the nineteenth century, to be followed by the discovery of benzene and of the liquefaction of chlorine and other gases. These apparently useless discoveries were destined at a later date to become the starting points of vast industries.

In these early days discoveries in chemistry found a means for their dissemination chiefly through the medium of the *Philosophical Transactions* of the Royal Society, and the investigations themselves were discussed at the meetings of the Society. Just as the Royal Society grew out of pre-existing societies, in which the social element was blended to a very considerable extent with the scientific, so our own Society had as forerunners "The Tepidarian Society" (of twenty-five), which drank only tea, and met at Old Slaughter's Coffeehouse in St. Martin's Lane, a society of which Davy was a member, as he was also of the Animal Chemical Society (of twelve), of which another member was Brande. In 1806 an attempt was made to found a Chemical Society, but it was not a success, being frowned on by Sir Joseph Banks, President of the Royal Society, who feared that "these various new-fangled associations will finally dismember the Royal Society, and not leave the old lady a rag to cover her."

Davy refers in a letter to W. H. Pepys, dated November 15, 1807, to the Chemical Club:—"Some things have happened in the Chemical Club which I think render it a less desirable meeting than usual, and I do not think you would find any gratification in being a member of it. . . . We sometimes meet only two or three" (Paris, "Life of Davy," i., 279).

The British Association for the Advancement of Science was founded in 1831, and brought together scientific men domiciled in various parts of the country, and at its annual meetings sorted them out into groups according to their own specific subjects. In this way the chemists in Section B assembled to discuss their various investigations and the difficulties met with in their prosecution

before proceeding to the formal publication of their work. These meetings, from their helpful nature, no doubt suggested the formation of a formal and central society ten years later, the chief object of which would be the communication and discussion of chemical papers. I refer later to the assistance given by the Association to our Society in its earlier days in the form of grants to enable abstracts of foreign papers to be published.

At a later date the meetings of Section B led to the founding of another chemical society or club (or "hive" of B's as they sometimes styled themselves). Our Library possesses some of their compositions, and I have come into the possession of several others, along with an album containing photographs of several B's dating between 1865 and 1870, no doubt during the period when Dr. W. J. Russell was its secretary. These I propose to present to the Library, and I hope that any Fellows of the Society or their friends who may possess any relics of this interesting small society may assist in rendering as complete as possible our collection of its records. The club was limited to twenty members, who united to their devotion to chemistry a strong conviction that in addition to the objects set forth in our charter and the best means of fulfilling them there were other ways of promoting the welfare of chemical science than those contemplated by the more formal society. They therefore dined together once a month during the Society's session, and in the summer an excursion was made into the country, guests being invited.

There were several poetic spirits who proved that there is no real hostility between a literary training and the scientific spirit. The poets-in-chief were Frederick Field, John Cargill Brough, and William Phipson Beale, and it is to Sir W. P. Beale that I am indebted for much information concerning the B's, and have been able to record the authorship of some of these *jeu d'esprit* with certainty. His recent book on crystallography, presented by him to the Library on its publication last year, shows that, besides his many-sided Parliamentary work, he is still a busy B and making honey of the true kind. Only two B's besides himself remain, so far as I can find out, namely, Profs. Odling and G. Carey Foster.

The rules of the club, headed by the appropriate emblem, were printed, as were also the card with the dates of the meetings for the session and the list of B's.

The successor to the B Club is the Chemical Club, and though it issues no rules or lists of members, flourishes under the energetic secretaryship of Prof. H. E. Armstrong with a nominal membership of fifty.

Fellows present may like to have some idea of the personal appearance of the founders of our Society, and I have been able to project upon the screen what to me is the most striking portrait of Thomas Graham, our first President, I have seen. I owe this to the kindness of Prof. J. M. Thomson, who has had the courage to entrust to me for the purpose of making the transparency the negative from which he prepared the exquisite platinotype print in the Jubilee Album. The Society realises but little how much it is indebted to Prof. Thomson's care and energy for the portraits of the Past Presidents in the Council Room and the priceless series of platinotype prints in the Jubilee Album. The only record of what he has done in this direction is a sentence on page 18 of the Jubilee Volume, which states that of the forty-four portraits in the album more than half have been executed by Prof. Thomson, of King's College. I believe it would have been more correct to have stated that nearly the whole of them were due to him.

[The portrait of the first Secretary, Robert Warrington, which hangs in the Officers' Room, was also exhibited].

To return to the foundation of the Society itself, it is interesting to note that from its very foundation it has laid stress on the importance of research, and President after President has insisted that, however it may seem to flourish financially or in other worldly ways, it is on the amount of research and on the vigour with which that is

prosecuted by its Fellows that the reputation and the true value of the Society must always depend.

In the statement of the objects to be aimed at by the Society, as amended at its meeting on March 30, 1841, we find that the establishment of a "Laboratory of Research" is specifically mentioned as one of the ulterior objects of the Society, in addition to a museum and library, and the communication and discussion of discoveries and observations.

At the first anniversary meeting the Report of Council states:—"The Council is fully sensible that the utility of the Society and its reputation in the scientific world will mainly depend on its publications" (1842).

Again, in 1845 the Council recognises it as a serious duty devolving on it to stimulate and encourage the zeal of the members by every means in their power, and recognises that there should be no unnecessary delay in the publication of papers, and that by pressing somewhat unreasonably on the time and goodwill of the Secretary six numbers of the *Memoirs and Proceedings*, consisting of forty communications, had been published during the year.

The *Memoirs and Proceedings* had been published at intervals according as materials came to hand, and it ought to be noted that several very important investigations were embodied in these early volumes, a fair number of which were carried out on the Continent. The first paper read at the first scientific meeting on April 13, 1841, was entitled "On the Preparation and Formation of Yellow Prussiate of Potash," by Prof. Liebig. The first volume contains papers "On the Atomic Weight of Carbon," by Redtenbacher and Liebig; "On the Radicle of the Cadocyl Series of Compounds," by Bunsen, as well as several by Ure, Stenhouse, Graham, and Fownes.

In 1848 the *Quarterly Journal* took the place of the *Memoirs*, and with it began the regular publications of the Society, which have continued ever since. In this year also the Charter of Incorporation was granted to the Society by Queen Victoria "on this second day of November, in the 12th year of our reign," when "The Chemical Society of London" became "The Chemical Society."

I have already stated that no mention of the Crimean War occurs in our records, but it is interesting to note that in 1854 the Council decided that lectures not exceeding five in number in any year should be given, and in making this arrangement to increase the interest in the scientific meetings the opportunity was again seized to impress on Fellows that it was not in the interesting nature of the meetings but solely on its publications that the position and character of the Society would depend.

In the report of the following year a sentence occurs which is equally true now, and may again be commended to the notice of Fellows, namely, "That the Library is a place of deposit for curious works upon chemistry and for pamphlets upon chemical subjects, which collected are of great interest, but separately are often of little or no value to their possessor."

Although discovered in 1856, a substance which was the forerunner of a multitude of others from the same source, and the origin of a vast industry which we hope may once more be ours, was first exhibited, together with some other coal-tar products, on March 31, 1857, to the Society, which then occupied its first set of rooms in Old Burlington House, where the Royal and Linnæan Societies were also located. This was followed next year by a change in the day of meeting from Monday to Thursday, so that all three societies might meet on the same day.

The Library had now (1860) become such an important part of the Society's possessions that a permanent librarian was appointed in the person of Henry Watts (whose portrait also has been brought here from the Officers' Room), a name known and revered by all who wanted to know anything that was to be known in chemistry as long as he maintained his connection with the Society, not only as its Librarian but as the Editor of its *Journal*, a connection that was only terminated by his death. He was elected

Editor in December, 1849, and died in June, 1884. To those who use his "Dictionary" (I mean the original and vigorous edition) it is rather quaint to find it recorded that the office of librarian "has been undertaken by Mr. Watts, a gentleman who is familiar with the literature of the science."

In 1862 the Society attained its majority, when its Fellows had increased from the original 77 to 360. Hofmann, then President, was able to declare that "by the number of our body, by the value of its contributions to science, by the increasing interests which our proceedings elicit, we have secured a respectable position in the world. We may look with some degree of satisfaction upon the achievements of our youth, and from the result of the past derive encouragement for the future."

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 12, March 20, 1916.

Influence of Hydrogen Peroxide on Germination.—E. Demoussy.—Some chemical reagents appear to possess the power of making the germinative power reappear in seeds which have lost it owing to age; chlorine, water, and hydrogen peroxide have been mentioned as being capable of producing this effect. The author has studied the action of hydrogen peroxide on cress seeds which were seven years old. These seeds when placed in distilled water, but not submerged, would not germinate at 27°, usually a favourable temperature for their development. But in dilute hydrogen peroxide germination began on the third day, and reached 30 per cent of the grains after ten days. On further diluting the solution the result was still better. Previous soaking, even for a very long time, in H₂O₂ is not effectual, but the reagent has to be actually present during the germination. Old seeds in pure water at 27° are invaded by microbes, the development of which is very rapid, beginning on the second or third day. This does not occur in hydrogen peroxide. At the temperature of the laboratory, varying from 10° to 14°, the results were not the same; all the seeds began to germinate about the sixth day. Thus seeds which are capable of germinating in the cold do not do so at 27°, a temperature which is very favourable to the germination of young seeds. At a low temperature the development of microbes is very slow, only becoming apparent towards the tenth day, after germination has begun. In old seeds the germinative energy is greatly diminished, and the development begins only after a relatively long time together with that of their parasites. Thus there is a struggle for oxygen, and the advantage rests with one or the other according to the conditions. When the seeds are placed in hydrogen peroxide this reagent opposes the evolution of the microbes but not that of the seeds, so that germination occurs at every temperature. The same seeds which did not germinate in pure water at 27° do germinate (in the proportion of 25 per cent) when placed in damp sand; this is because the surface of aeration is greater and the action of oxygen is facilitated. Thus old seeds may have preserved their germinative power and yet not germinate in conditions favourable for young seeds, if these conditions are also favourable for the development of parasitic micro-organisms which asphyxiate them. The seeds germinate if their oxidation is facilitated and if the evolution of the micro-organisms is retarded. When seeds are tested for germinating power in the laboratory some may be found to be bad which would

prove to be of medium quality when introduced into the soil. This is a result which has already been reached by practical men, especially with beetroot seed.

Modification of Method of Sterilising Drinking Water by Sodium Hypochlorite.—V. Ferrand.—To sterilise water by sodium hypochlorite the reagent is shaken with the water which is allowed to stand for at least an hour, and then the free chlorine is neutralised by sodium hyposulphite. When hydrogen peroxide is added to sodium hypochlorite the reaction which takes place is represented by the equation $\text{NaClO} + \text{H}_2\text{O}_2 = \text{ClNa} + \text{H}_2\text{O} + \text{O}_2$, and the author has found that hydrogen peroxide can conveniently be used to replace hyposulphite in the sterilisation of water. The destruction of microbes of the *coli* group is thus effected much more quickly than by the usual method.

NOTICES OF BOOKS.

Kelly's Directory of Chemists and Druggists. 13th Edition, 1916. London: Kelly's Directories, Ltd., 182, 183, 184, High Holborn, W.C. Price 25s.

THIS valuable directory, just issued, has been corrected up to the latest date. It includes the names and addresses not only of chemists and druggists, but also of manufacturing chemists, wholesale druggists, dyers, dentists, veterinary surgeons, hospitals, surgical instrument makers, photographers, photographic material makers, and all other trades connected therewith in England, Scotland, and Wales, and the principal towns in Ireland, the Isle of Man, and Channel Islands.

The work runs into nearly 800 pages, and the system of cross indexing enables the information to be gained with a minimum of labour.

At the present time, when the state of the chemical and allied industries is of such supreme importance, the directory is very welcome, and the publishers are to be congratulated at having overcome the abnormal difficulties connected with its issue during the war.

NOTES AND QUERIES.

"Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Nitre Cake—As we are interested in the question of nitre cake as a substitute for sulphuric acid, we shall be greatly obliged for the names of the firms who are endeavouring to make this.—HARDING, RICHARDSON, RHODES, and Co., Ltd.

MEETINGS FOR THE WEEK.

MONDAY, 15th.—Royal Society of Arts, 4.30. (Cantor Lecture). "Vibrations, Waves, and Resonance," by J. Erskine-Murray.

TUESDAY, 16th.—Royal Institution, 3. "Unconscious Nerves—Their Functions in Internal Life," by Prof. Charles S. Sherrington.

Institution of Petroleum Technologists, 8. "Petroleum Refining," by A. Campbell.

WEDNESDAY, 17th.—Royal Society of Arts, 4.30. "Hindu Hand-painted Calicos of the Seventeenth and Eighteenth Centuries, and their Influence on the Tintorial Arts of Europe," by G. P. Baker.

Microscopical, 8. "Some Suggestions regarding Visual Efficiency in the Use of the Microscope and other Optical Instruments," by J. W. Purkiss. "A Case of Apparent Intelligence exhibited by a Marine Tube-building Worm, *Terebella conchilega*," by A. T. Watson. "Alien Oligochaets in England—*Dichogaster lageniformis*, sp. n.," by Rev. H. Friend.

THURSDAY, 18th.—Royal Institution, 3. "Flint and Flint Implementations," by Sir Ray Lankester.

FRIDAY, 19th.—Royal Institution, 5.30. "The Movements of the Earth's Pole," by Col. E. H. Hills.

SATURDAY, 20th.—Royal Institution, 3. "The Finance of the Great War—New Problems and New Solutions," by Prof. H. S. Foxwell.

THE CHEMICAL NEWS.

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THE CHANGES IN PHYSICAL PROPERTIES OF ALUMINIUM WITH MECHANICAL WORK.*

II.—SPECIFIC HEATS OF HARD AND SOFT ALUMINIUM.

By F. J. BRISLEE, D.Sc.

It has been previously shown that the density of aluminium decreases with mechanical work (*Trans. Faraday Soc.*, 1913, ix., Parts 1 and 2). The change in density is greater, the greater the amount of work done upon the metal. Annealing brings about the reverse change, the density increasing after annealing. Microscopic examinations of polished and etched specimens show an absence of structure; i.e., they are amorphous, the well-defined crystalline structure of cast and slowly cooled aluminium or thoroughly annealed aluminium has disappeared entirely under the influence of mechanical work.

When soft aluminium is worked, either rolled into rods, or sheet, or drawn into wire, the tensile strength increases, but the elongation under stress rapidly decreases. By continuing to work the metal a high tensile strength is ultimately reached. The metal has, however, lost its ductility, and become brittle, and will not stand being bent at right angles without fracturing.

The change in physical properties of the metal with work is explained by the assumption that it passes into an allotropic or amorphous state.

Cohen (*Ibid.*, 1915) has shown that many metals pass, more or less readily, into allotropic modifications, the two or more forms differing from each other in density and other physical properties. The method of converting a metal into its allotropic modification differs for each metal; in one case the metal was turned into fragments in a lathe, in another case the metal was made the electrodes of an electrolytic cell, the electrolyte containing free nitric acid.

The change which aluminium undergoes when subjected to excessive mechanical work may result in the formation of an amorphous phase, or in the conversion, partially at any rate, into an allotropic modification; the increase in hardness, difference in strength, and changes in physical properties being proportional to the quantity of the amorphous phase present. The hardness of iron and steel is probably due to the amorphous phase which is produced by the different methods of treatment in the process of hardening.

The physical properties of an element are different for the crystalline and amorphous states, and different for the various allotropic modifications. The change—

Crystalline $\rightleftharpoons$ Amorphous

is accompanied by only a small change of energy, but the change—

Allotrope I. $\rightleftharpoons$ Allotrope II.

is usually accompanied by a measurable change of energy.

The specific heat varies with the physical state, the specific heat of the amorphous variety being usually higher than the crystalline. It follows, therefore, that the specific heat will depend upon the conditions of the metal, and be different for cast, annealed, or worked metal. The recorded values for the specific heats of those elements which exist in well-defined allotropic modifications are higher for the amorphous variety.

Element.	Specific heat.	
	Crystalline.	Amorphous.
Carbon	0.1128	0.2040
Silicon	0.165	0.2140
Boron	0.2518	0.3066
Tin	0.0542 white	—
Tin	0.0589 grey	—

The mean specific heat of aluminium has been determined by Tilden (*Proc. Roy. Soc.*, 1903, lxi., 220; *Phil. Trans.*, A, 1903, cci., 37), Voigt (*Wied. Ann.*, 1893, xlix., 709), Richards (*CHEMICAL NEWS*, 1893, lxxviii., 58, 69, 82, 93), and others, and more recently by Harker and Greenwood (*W. P. L. Report*, 1911, p. 54). The results vary somewhat, as the following figures show:—

Temperature.	Specific heat.	Observer.
15°—185°	0.2189	Tilden
20°—100°	0.2145	Voigt
0°	0.2220	Richards
18°—200°	0.2187	Harker and Greenwood
18°—300°	0.2264	
18°—400°	0.2328	

Harker and Greenwood's results were obtained with cast metal enclosed in silicon tubes, the specific heat being determined to a temperature above the melting-point of the metal.

A series of comparative experiments were made with a view to determining the specific heat of aluminium in the worked and annealed condition. The aluminium employed was of a high degree of purity, containing 99.6 per cent aluminium. The impurities present were silicon, iron, and a trace of copper. The metal was drawn into square bars of 1-inch side, into 5/8-inch rod, and into wire 0.084 inch in diameter. The wire was extremely hard, had a high tensile strength, but could not be bent or twisted without fracturing. The square rod was cut into 6-inch lengths, and a hole 3 inches deep was drilled in the centre of one end. The bulb of the thermometer was placed in this hole during heating. The bars were heated in an electric tube furnace for temperatures above 100° C. For a temperature of 100° C. the heating was effected in a jacketed heater, through which steam was passed. The wire was made into bundles weighing from 100 to 300 grms. each, the weight in all the experiments being such as to give a considerable rise of temperature in the calorimeter. The specific heat was determined in a copper calorimeter fitted with a stirrer and lid. The calorimeter vessel was contained in an outer water-jacketed vessel to shield it from external radiations. This in turn was shielded by a wooden case. The calorimeter contained 1000° to 2500 grms. of water, according to the rise of temperature expected. The water equivalent of the calorimeter was calculated from its weight. The rise of temperature was measured with a thermometer divided into 1/10°, and capable of being read to 1/100°, and also with a Beckmann thermometer graduated in 1/100°, which could be read by aid of a lens to 1/1000°. The temperature of the metal was measured with a nitrogen-filled mercury thermometer and with a platinum rhodium thermo-couple. Repeated determinations were made over the same range of temperature. It was found possible to reproduce the results to within a comparatively small difference. The experiments for the range 300° C. to 20° C gave the following results for annealed aluminium:—

		Mean specific heat S /20.
Mean of 23 determinations	0.2354	
Extremes { Highest	0.2392	
{ Lowest	0.2329	
The mean error of each measurement is	± 0.0016	
The mean error of the mean	± 0.00033	
For the range 200° C. to 20° C.—		
Mean of 12 experiments	0.2240	
Extremes { Highest	0.2264	
{ Lowest	0.2221	
The mean error of each measurement	± 0.0014	
The mean error of the mean	± 0.0004	

* A Paper read before the Faraday Society, May 9, 1916.

The determinations were made under constant conditions; the transference of the metal from the heater to the calorimeter was effected as rapidly as possible. Every precaution was taken to avoid loss of water from the calorimeter through splashing and through the formation of steam.

The above values agree well with those found by Tilden (*loc. cit.*), who found:—

Range.	Specific heat.
15°—185°	0·2189
15°—434°	0·2356

The values found by Harker and Greenwood (*loc. cit.*) are different from the above, viz.:—

Temperature.	Specific heat.
200° C.	0·2187
300° C.	0·2264

The explanation of the difference may be found in the fact that they employed cast metal for the determination. The specific heat differs for the metal in the cast, annealed, and worked condition.

In the course of the preliminary determinations it was found that the values obtained in repeat experiments varied from the values obtained later on when the metal had become more thoroughly annealed, and it was not until the various bars had been thoroughly annealed that concordant values were obtained. The specific heat of aluminium depends upon its previous treatment, both thermal and mechanical. This was found for sodium by E. Griffiths (*Proc. Roy. Soc., A*, 1914, lxxxix., 561), but it was not investigated further. In order to determine the specific heat of hard worked aluminium, a quantity of the metal was rolled into rod and drawn into wire, without annealing and with the maximum draught possible, to 0·084 inch diameter.

The resulting metal had a density of—

$$\delta \frac{15.5}{4} = 2.7063$$

as a mean of 10 determinations. It was brittle, and broke readily when bent at right angles, but had a high tensile strength, viz., 18·7 tons per square inch, when tested in a tensile testing machine. The wire was cut into 7-inch lengths, thoroughly cleaned, and made up into loose bundles, weighing 300 grms. each, which were used for the determination of the specific heat. The values obtained were:—

Range 100°—20° C.	Mean specific heat S _{1/20} .
Mean of 7 determinations	0·2220
Extremes { Highest	0·2239
{ Lowest	0·2213

For these determinations seven bundles of wire were used, varying in weight from 278 grms. to 335 grms., and the experiments gave extremely consistent values. After each experiment the bundles were drained and placed in a steam-oven to dry thoroughly before using again for a further experiment. It was found, however, that the specific heat was less after heating than for the new metal. After heating for 10 days to 100° C. in a steam-oven, the specific heat approximated to that found for the annealed metal. Lowry has found that aluminium changes in density when heated to 120° C., a fact previously found by the author. The following figures were obtained:—

Weight of aluminium, grms.	1st value—specific heat, new metal.	2nd value—specific heat after 10 days' heating to 100° C.
318	0·2211	0·2170
278	0·2222	0·2150
302	0·2224	0·2186
298·5	0·2214	—
319	0·2239	—
300	0·2219	—
335	0·2213	0·2193

From these results it would seem that the amorphous phase began to change into the crystalline even at 100° C. Now if the hardness is dependent upon the amorphous phase, the wires should show a change in tensile strength after heating to 100° C. The wire was allowed to remain in the steam-oven at 100° C. for a period of ten weeks, and the tensile strength determined, then it was again allowed to remain for a further period of ten weeks, and the tensile strength re-determined. The following results were obtained:—

	Tons per square inch.
Tensile strength of wire 0·084 inch diameter, as worked (mean of 7 tests)	18·7
Tensile strength after 10 weeks at 100° C. (mean of 7 tests)	14·4
Tensile strength after 20 weeks at 100° C. (mean of 10 tests)	13·7

In order to still further confirm this drop of tensile strength at the comparatively low temperature of 100° C. a further lot of the aluminium was drawn down to 0·010 inch diameter without annealing and employing the maximum draught at each reduction of diameter by passage through the wire dies. The resulting wire was extremely brittle when bent, but had a high tensile strength when subjected to a pull. The coil of wire was divided, one portion being kept as worked, the other portion was heated in a steam-oven to 100° C. for ten weeks, and the tensile strength determined. The portion of the original wire which was not heated gave the same tensile strength as it did, showing that no change occurred at ordinary temperatures. The following results were obtained:—

	Tons per square inch.
Tensile strength of 0·010 inch wire as worked (mean of 5 determinations) ..	18·4
Tensile strength after heating for 10 weeks at 100° C. (mean of 6 determinations)	13·2

After this treatment the wire became quite serviceable, and was capable of being twisted and bent. It follows, therefore, that aluminium undergoes very considerable structural changes, even at as low a temperature as 100° C. within a moderate time.

Further, it follows that the specific heat varies with the physical condition to an easily measurable degree, and therefore any determination of the specific heat must be made upon metal the history of which is definitely known.

The greater proportion of the specific heats recorded are fortuitous (*vide* Cohen, *loc. cit.*), and the accurate experimental determinations are vitiated by the indefinite state of the metal. This applies to the extremely accurate work of E. H. and E. Griffiths (*Proc. Roy. Soc., A*, 1913, lxxxviii., 549).

The results obtained for the specific heat of worked aluminium are concordant among themselves, but they probably represent results obtained from metal in an indefinite and varying state. The metal was worked, as far as it was possible to do so, by drawing into wire. Any further attempt to draw to a still finer wire resulted in fracture, the metal having insufficient ductility remaining to allow the reduction in diameter necessary to pass through the die. Up to the present it has not been possible to completely convert aluminium into the amorphous form by drawing. It is possible that extreme work, such as stamping until the metal falls to powder, will produce a much larger proportion of amorphous aluminium, and may even transform it wholly into the amorphous phase. Experiments are being made in this direction, but owing to the difficulty of preparing quantities of the metal in the amorphous state and the uncertainty of the proportions of amorphous and crystalline in any sample of metal, it is obvious that further investigation is necessary before it is possible to state the specific heat definitely for the amorphous phase.

It is also evident that the reverse change takes place with extreme slowness, so far as visible structural changes are concerned. Rosenhain has observed that aluminium anneals with great slowness, and this is confirmed by the author's observations.

The amount of cold work which can be done upon aluminium is limited by the formation of the amorphous state. Microscopic examination of polished and etched specimens taken at various stages during cold working shows that the crystalline structure disappears at a very early stage in the working, and unless the metal is annealed it will become fatigued, developing a species of "Forcierre-krankheit." Aluminium which has been subjected to excessive cold work shows an entire absence of structure, and has the appearance of a metal which has flowed and passed into a vitreous state. The reverse change takes place with extreme slowness, and the ordinary annealing process does not change the structure from amorphous to crystalline. Aluminium annealed at a temperature of 500° C. for ten hours appears to be "dead soft," and has its maximum elongation; nevertheless, it is still largely amorphous in structure when examined microscopically. Aluminium which has been annealed in this way without affecting the structure or only slightly altering it, hardens very rapidly when additional cold work is done upon the metal. The primitive crystals are transformed into the amorphous state much more readily than the larger crystals which are developed by annealing. The results of the specific heat determinations renders the conclusion probable that under the influence of cold work aluminium is transformed into an amorphous variety. The conclusion is only put forward tentatively, since, at present, there is no means of determining the amount of each phase present in the hard metal, hence the results which have been obtained for hard aluminium are for a metal consisting of a mixture, in unknown proportions, of the two forms of the metal. Long annealing seems to yield a metal in the most definite condition; cast metal is greatly influenced by the casting temperature and rate of cooling.

THE EXTRACTION AND SEPARATION OF THE RADIO-ACTIVE CONSTITUENTS OF CARNOTITE.*

By H. M. PLUM.

(Continued from p. 225).

Details of the Method Used in Treating Kilogram. Lots of Carnotite.

SINCE the foregoing experiments seemed to indicate that the treatment of the ore with sodium carbonate solution gave most satisfactory results, this method, therefore, was carefully investigated. Various experiments were made on 100 grm. lots to ascertain, first, what concentration of sodium carbonate solution was most effective, and, second, what conditions of temperature gave best results. The mass of ore was then increased to a kilogram., and after five or six of these had been worked over a final kilogram. was treated in the following manner:—

One kilogram. of carnotite and 400 grms. of chemically pure anhydrous sodium carbonate were mixed with about two litres of water and heated to boiling for several hours. This mixture was frequently stirred to secure uniform heating, water being added as the mass thickened. While still hot it was filtered under suction through a filter cloth and the filter cake washed with hot water. The washing was a slow process, but attempts in preceding experiments on boiling up the residue with water had proved that it made the mass more colloidal, and, consequently, more difficult to filter. Decantation processes were also abandoned because of the slowness with which the mud-

like material settled. The brown filtrate thus obtained contained most of the uranium, less than half of the vanadium, and the unchanged portion of the sodium carbonate. After attempts to separate the uranium from the carbonate solution by means of a variety of reactions a very simple and effective method was finally discovered. It was found that when the carbonate solution was evaporated so that the solution became nearly saturated with sodium carbonate, the uranium settled out as a beautiful yellow product, easily filtered from the hot solution. This substance, which on analysis proved to be uranyl sodium carbonate, $\text{UO}_2\text{CO}_3 \cdot 2\text{Na}_2\text{CO}_3$, was quite heavy and settled quickly. To obtain the maximum recovery of this compound the evaporation was continued up to the point at which the sodium carbonate just began to crystallise out, and the hot solution was filtered at once. Strong suction left the uranyl sodium carbonate almost free from impurities, so that very little if any water was required in washing to give a relatively pure product. The amount of dry precipitate obtained in this way from each kilogram. of carnotite concentrate varied from 85 to 90 grms. In this final kilogram. lot the weight of the uranyl sodium carbonate was 88.1 grms.; this was 88 per cent of the total amount of uranium in the ore. An examination of the filtrate from the uranyl sodium carbonate precipitate showed it still contained 2 per cent of the uranium. When the residue from the first carbonate extraction was treated again with 300 grms. of sodium carbonate under conditions similar to the above the amount of uranium carried in this filtrate was too small to be recovered as uranyl sodium carbonate. On examining the filtrate, however, the uranium found was only 2.8 per cent of the total amount in the ore. It thus appears that a second treatment with sodium carbonate solution is an unnecessary step in the operation.

The identity of the yellow compound referred to in the preceding paragraph was established by analysis. Some of the material was heated at 125° to constant weight. The loss, which amounted to about 1 per cent, was due undoubtedly to moisture held mechanically. The residue of silica, &c., left on dissolving some of the compound in dilute sulphuric acid amounted to about 0.3 per cent. The determination of the uranium was made by reducing a weighed amount of the yellow body with zinc and sulphuric acid and then titrating with potassium permanganate. Sodium was determined by removing the uranium with ammonium hydroxide and then converting the sodium compound into the sulphate. This analysis, as indicated by the figures below, proved the compound to be uranyl sodium carbonate:—

Results of Analysis.

Loss on heating at 125° ..	0.98 per cent
Insoluble residue	0.31 "

Composition of the Portion Free from Volatile and Insoluble Matter.

	Found.	Calculated for $\text{UO}_2\text{CO}_3 \cdot 2\text{Na}_2\text{CO}_3$.
Uranium ..	43.65	43.97
Sodium ..	17.07	16.96

The uranyl sodium carbonate obtained by the same method on other kilogram. lots had been carefully examined to see if any of the other radio-active substances had been carried along with the uranium. Portions of the compound were dissolved and attempts made to find polonium, radium, ionium, and actinium by methods described in later paragraphs of this paper, but in none of these experiments was there found any active substance other than uranium. The solution filtered from the uranium carbonate contained a large excess of unchanged soda, together with the sodium vanadate. This solution was evaporated until it became saturated with the soda and then cooled to 0°. Sodium carbonate is more than six times as soluble at 100° as at 0°, so that large masses of crystals were obtained when the boiling saturated solution was cooled.

* Journal of the American Chemical Society, xxxvii., No. 8.

With a little ice water these crystals could be washed nearly free from the vanadium which remained in solution. By further evaporation other crops of crystals could be obtained and in this way most of the uncombined soda recovered. The sodium carbonate thus obtained could be used repeatedly in treating the original ore, and thereby a great saving of that compound be realised. As vanadium can be obtained from its solutions by well-known methods the sodium vanadate solution left after the removal of the uranium and the excess of sodium carbonate was studied only in so far as to find that none of the radio-active elements were present in it.

After the original ore had been treated with a solution of carbonate of soda the next step was to boil the residue with hydrochloric acid. In preceding experiments it had been found that if dilute acid were used only in such quantities as to break up the easily decomposed carbonates and not in sufficient amounts to bring into solution any of the iron or vanadium the yield of radium was not more than 60 to 65 per cent of the total amount in the ore. By boiling with more concentrated acid the percentage of radium recovered could be greatly increased. Further, three consecutive treatments with boiling hydrochloric acid, made by mixing one volume of concentrated acid with about three volumes of water, still left radium in the residue, most of which could be removed by boiling the residue with nitric acid diluted with three or four times its volume of water. Consequently a single treatment with hydrochloric acid, followed by one with nitric acid, was found to be the most satisfactory method to follow. In accordance with these results the residue left from the carbonate treatment of the last kilogram of ore was boiled with 400 cc. of concentrated hydrochloric acid diluted with with two or three times its volume of water. The heating was continued for about eight hours, water being added as it disappeared by evaporation. The hot mixture was then filtered and the filtrate evaporated to a smaller bulk. This solution was then carefully examined for radio-active elements. 50 cc. of a 1 per cent bismuth nitrate solution were added and completely precipitated with hydrogen sulphide, the excess of which was removed from the filtrate by boiling it after the sulphides had been collected on a filter. These sulphides were then dissolved in concentrated nitric acid, sulphuric acid was added to the solution, and the lead was separated from bismuth by the customary analytical methods. The lead sulphate removed in this way contained the radio-lead. The bismuth in the filtrate was precipitated with ammonium hydroxide and after filtering and washing it was dissolved in hydrochloric acid. It was in this solution that most of the polonium appeared. To the filtrate from the sulphides 3 or 4 cc. of concentrated sulphuric acid were added, which caused the precipitation of radium and barium as sulphates. Small amounts of barium chloride were now added, and a second and third precipitation was made for the purpose of carrying down the radium and actinium more completely, especially the latter. The filtrate from barium sulphate was then neutralised with ammonia up to the point of precipitation of the hydroxides, 5 to 10 grms. of cerium chloride or nitrate were added, and the cerium was precipitated with oxalic acid. This was a troublesome process, as it necessitated the use of large amounts of oxalic acid before precipitation of cerium oxalate could be brought about. The activity of the cerium oxalate precipitated in this way was much too little to account for all the ionium, and it was the lack of radio-activity at this point which led to the belief that the ionium had not yet been removed from the residue. When some thorium nitrate was added to this filtrate instead of cerium and a precipitation of thorium oxalate was made with oxalic acid no better recovery of ionium was obtained.

The residue from the hydrochloric acid extraction was next treated with 200 cc. of concentrated nitric acid diluted with about a litre of water. This was kept at boiling temperature for a day, at the end of which time the mass was filtered. The resulting filtrate was examined for

radio-active elements by methods similar to those used in studying the hydrochloric acid filtrate, but none of these elements could be found except radium. On the addition of a few cc. of sulphuric acid to the filtrate a precipitate formed, which showed the presence of considerable activity. In short, nitric acid always brought into solution soluble matter containing radium which hydrochloric acid was incapable of dissolving out of the ore.

The final step in the process was that which involved the use of sulphuric acid. The residue left from the foregoing extractions was mixed with twice its weight of sulphuric acid which had been diluted with water in the proportions of about five of acid to four of water. This was slowly heated and the temperature so regulated that most of the acid fumed away. If the heating was not excessive, on digesting the resulting mass with hot water the residue was pure white, for all vanadium and iron remaining in the ore were completely removed by this process. It was in this filtrate that most of the ionium was found. To remove it about 10 grms. of cerium nitrate were added and the excess of sulphuric acid was neutralised with ammonium up to the formation of a small amount of the hydroxides. A large quantity of oxalic acid was then added, which dissolved the slight hydroxide precipitate and after some time precipitated the cerium as oxalate. This process was difficult to carry out, for it seemed impossible to precipitate the cerium oxalate until the solution was almost saturated with oxalic acid. Keeping the solution well stirred and rubbing the sides of the containing vessel with a glass rod aided considerably in the precipitation. In order to recover the ionium more completely a second portion of cerium nitrate was added to the solution and a second precipitation of cerium oxalate was obtained. The methods used in concentrating the ionium and in measuring its activity are given later in the special paragraph on ionium.

Radium.

The complete method of treating the ore, as described in preceding paragraphs, gave a good recovery of radium, the greater part of which appeared in the solution obtained from the hydrochloric acid extraction. To get the best results it was necessary, however, to follow the hydrochloric acid treatment with a nitric acid extraction, because the latter always dissolved material insoluble in hydrochloric acid, which still contained about 8 to 10 per cent of the radium. In working up the last kilogram of ore the barium radium sulphate precipitate obtained from the hydrochloric acid filtrate weighed 7.36 grms., and that from the nitric acid solution 0.45 gm. By the addition of successive small equivalent amounts of barium chloride and sulphuric acid 9.30 grms. of barium sulphate were precipitated in the filtrates from the first precipitates of this substance.

The percentage of recovery of radium was determined by comparing the activity of the original ore with that of the radium barium sulphate, the emanation method being used for the purpose. To do this $\frac{1}{2}$ gm. of the original ore, after being mixed with 5 or 6 grms. of anhydrous potassium sulphate, was carefully fused in a hard glass test-tube and then made air-tight. After several days this mass was again fused, the emanation transferred completely to an emanation electroscope (without the use of water), and the time of discharge observed. By knowing the exact interval the tube was sealed, the time of discharge for the maximum amount of emanation could be calculated from the known rate of decay and growth of radium emanation. In a similar way the activity of the radium barium sulphate was obtained, except that in this determination only 0.0150 gm. of material was used in each fusion. On comparing these results it was found that 89.9 per cent of the total radium had been recovered in the barium radium sulphate precipitated from the hydrochloric and nitric acid solutions. The barium sulphate obtained by adding small amounts of barium chloride to the filtrates, as described above, was only

slightly active, and held but 2.7 per cent of the radium. The residue left after all extraction processes contained only 4.2 per cent of the total radium contained in the ore. This leaves 3.3 per cent of the radium unaccounted for.

(To be continued).

EXPERIMENTS ON THE NATURE OF THE PHOTOGENIC PROCESSES IN THE LAMPYRIDÆ.

By F. ALEX. McDERMOTT,
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DURING the summer of 1914 the writer made some tests along the same line as described in the paper by Harvey (see p. 219), and he also attempted to obtain evidence of the breaking down of nucleic acids during the photogenic process, as suggested by Lund (*Yourn. Exper. Zool.*, 1911, xi., 415). While the results are mainly negative they are of interest as confirming Harvey's experiences. The obvious limitations to such work, owing to the restricted amount of material available at one time, is a serious handicap to very extensive results. Most of the present writer's experiments were made on material prepared from *Photinus pyralis* and *P. castus*; some of the material from the former species had been collected at Washington, D.C., in the summer of 1911, and after drying *in vacuo* over sulphuric acid had been sealed *in vacuo* in small flasks. This latter material was very kindly supplied to me by Prof. J. H. Kastle, Director of the Kentucky Agricultural Experiment Station. It was apparently as active as when first prepared.

Extractions were made in oxygen-free natural gas. After grinding, the tissue to be tested was placed in a small separatory funnel, which had been filled with gas which had been passed through pyrogallol solution; the washed gas was allowed to pass through the funnel for some time to sweep out any air which may have entered when the tissue was placed in the funnel. For the filtering a vacuum desiccator was fitted up with a small beaker, a wire funnel support, and a small funnel with a folded filter. The desiccator was connected to the gas supply for some time in order to remove all the air. The solvent to be used was placed in a small Erlenmeyer flask provided with a tightly fitting stopper bearing two small-bore stopcocks. The washed gas was passed through this flask for some time after the solvent had been run in, and the solvent was then heated slowly to the boiling-point and kept boiling quietly for about a minute, when it was allowed to cool slowly in a current of the gas (except in those cases in which it was used hot). When cool both stopcocks were closed and the outgoing tube connected to the inlet of the separatory containing the material to be tested; both tubes were well blown out with the gas before connection and kept surrounded by a current of gas while being connected; the outgoing stopcock on the flask and the ingoing on the separatory were then opened, then the ingoing stopcock on the solvent flask, and finally the outgoing on the separatory, the solvent being run into the separatory by the pressure of the gas, when the small flask was inverted. The stopcocks on the separatory were then closed and the solvent flask disconnected. The separatory was shaken thoroughly so that the tissue would be fully exposed to the action of the solvent; in some experiments filtration was done immediately while in other cases the tissue was allowed to stand in the solvent for some time, usually with occasional shaking.

Fifteen to twenty of the dried luminous segments, weighing about 0.05 to 0.07 gm., were usually used in a test. The filtrate and residue were usually tested by first exposing to the air and then by adding hydrogen peroxide (3 per cent solution), always in a dark room, the eyes being allowed to become accustomed to the darkness for at least

ten minutes before applying the test. In no case was the emission of light from the filtrate observed, though in short cold extractions with alkali some activity of the residual material was noticed, due to larger fragments of the material which had not been thoroughly penetrated by the solvent.

The following are some of the combinations which were used:—

1. 15 organs; 25 cc. 0.15N H_2SO_4 ; solvent used cold and allowed to stand fifteen minutes after shaking before filtration. No light at any stage.

2. 15 organs; 20 cc. 0.03N NaOH; solvent used cold and allowed to stand fifteen minutes after shaking before filtration. No light on adding solvent to tissue; faint light on running liquid on filter. Filtration very slow; no light on testing residue and filtrate four hours later.

3. 15 organs; 20 cc. 0.05N NaOH; solvent used cold and filtered immediately after shaking. No light at any stage.

4. 15 organs; 25 cc. 0.001N NaOH; organs crushed rather than ground; solvent applied hot and filtered immediately after shaking. No light at any stage.

5. 4 repeated, using cold alkali; larger pieces of tissue glow on treatment of residue with 3 per cent H_2O_2 on filter; no light from fine material on the filter nor from the filtrate. A very active catalase went into solution in the alkali in this experiment.

All the extracts had the characteristic odour of the insect, which was intensified by the alkali.

A considerable number of experiments were run using alkaline solutions as solvents, with the view that if nucleic acids were present, as suggested by Lund, and were active in light production they might be thus gotten into solution; in no case was an active extract obtained. To examine this point further, determinations of the total nitrogen in the insects and in the luminous organs, and of the nitrogen, phosphoric acid, and carbohydrates in the extracts were attempted. For the determination of the total nitrogen in the insects and in the luminous apparatus dried specimens of *Photinus castus*, collected in Pittsburgh, Pa., were used; this species is quite closely related to *P. pyralis*, and it is unlikely that there would be any wide difference in the proportion or distribution of the nitrogen in them.

The mean of two determinations of the total nitrogen in the luminous tissue showed 13.6 per cent, while the mean of two determinations on the remainder of the insect showed 10.3 per cent; this would indicate about 11 per cent N for the whole insect, calculated on the relative weights of the luminous segments and the remainder of the insect. All weights refer to the tissue dried *in vacuo* over sulphuric acid. The low figure for the total nitrogen of the insect is probably accounted for by the relatively large amount of chitin, while the high figure for the luminous tissue is undoubtedly due to the deposits of uric acid or closely related compounds which form the so-called reflecting layer, constituting the larger part of the bulk of the dry material from the luminous segments.

To test the possible effect of the photogenic processes on the amount of soluble nitrogen, phosphoric acid, and carbohydrate two experiments were run in parallel, using the tissue of *Photinus pyralis*. In the first test (A) 0.146 gm. of the ground dry tissue was treated with 20 cc. of hot 0.075N H_2SO_4 in natural gas; 1 cc. of 3 per cent hydrogen peroxide and 20 cc. of water were then added, the mixture boiled and filtered and the filtrate and washings made up to 50 cc. In the second (B) 0.179 gm. of the ground dry tissue was treated with 1 cc. of 3 per cent hydrogen peroxide and 20 cc. of water in the air, and allowed to stand till the action and light-emission had ceased; 20 cc. of 0.075N H_2SO_4 were then added and the solution boiled, filtered, and made up to 50 cc. By this means the material in the first test (A) was kept from light production, while in the second test (B) the light-producing power was expended. The nitrogen was determined in 25 cc. portions of each of these filtrates, while a

portion of the remainder was used for the titration of P_2O_5 with uranium acetate. Tests for optical activity were negative on both filtrates, which is taken to indicate the absence of significant quantities of carbohydrates. The results of the N and P_2O_5 determinations are given below:—

Test.	Per cent of weight of dry tissue taken.	
	N in solution, by Kjeldahl.	P_2O_5 in solution, by uranium acetate.
A	4.81	0.515
B	4.14	0.420

These figures do not show as great a difference as might be expected were the photogenic process accompanied by any extensive breaking down of nucleic acids, and the differences indeed are in the opposite direction to what would be expected under such circumstances.

From the evidence at hand, therefore, it seems that the deposits of purine substances which form the so-called reflecting layer of the photogenic organs of the Lampyridæ cannot be traced satisfactorily to the breaking down of nucleic acids. In agreement with the work of Harvey, reported in his paper (p. 219), dilute acid and alkaline solutions, hot or cold, fail to extract a light-producing substance from the dry tissues of these insects, even when used in the entire absence of oxygen, and such solutions rapidly destroy the photogenic activity of the dry tissue. —*Journal of the American Chemical Society*, xxxvii., No. 2.

INTERNATIONAL INSTITUTE OF AGRICULTURE.

BULLETIN OF AGRICULTURAL AND COMMERCIAL STATISTICS.

THE last number of the *Bulletin of Agricultural and Commercial Statistics* published by the International Institute of Agriculture contains information relating to areas sown and prospects of the crops in the Northern Hemisphere. As regards autumn sowings of cereals (1915-16 crop) the most important of the new figures in the present bulletin are those of wheat in British India (12,234,262 hectares, or 94.4 per cent of last year's area, and 103.5 per cent of the average of the preceding five years), and in Japan 502,107 hectares, or 111 per cent of last year's area, and 104.6 per cent of the average of the preceding five years), while the area under barley in Japan is estimated at 1,258,258 hectares, or 96 per cent of last year's, and 97.5 per cent of the preceding five years' average. There are no other important alterations shown as compared with areas stated in the March bulletin.

The state of these autumn sown crops is good in Italy, Roumania, and Egypt, satisfactory on the whole in France, Switzerland, the United States, British India, Japan, and Algeria, but in Great Britain the season is very backward.

Dealing with current harvests, preliminary estimates of the yield of maize in Argentina amount to 40,930,000 quintals, or 47.6 per cent of that of last year (an exceptionally abundant crop), and 84.1 per cent of an average of the previous five years.

By including these data from Argentina with the maize crops of the Northern Hemisphere the total yield of 1915 (and in the Southern Hemisphere of 1915-16) may be stated for the following countries:—Hungary, Spain, Italy, Roumania, European and Asiatic Russia, Switzerland, Canada, United States, Japan, and Argentina, giving altogether 946,761,150 quintals, or 105.7 per cent of last year's yield in these countries, and 100.8 per cent of that shown by an average of the preceding five years.

In the Commercial Section the *Bulletin* contains tables of imports and exports, of stocks and prices, for cereals and cotton, on the principal markets, together with information as to rates of ocean freight likewise on cereals and cotton, by the most frequented routes.

ARSENIOUS OXIDE AS AN ALKALIMETRIC STANDARD.

By ALAN W. C. MENZIES and F. N. MCCARTHY.

THE fact that arsenic acid can be estimated volumetrically with an exceedingly sharp end-point (Menzies and Potter, *Journ. Am. Chem. Soc.*, 1912, xxxiv., 1452) suggested the possibility of the employment of this acid for purposes of standardisation in alkalimetry. It is well known that arsenious oxide is a most desirable starting material in oxidimetry, and that the arsenious acid-iodine titration is one of the most accurate of the processes of volumetric analysis (*cf.* Washburn, *Ibid.*, 1908, xxx., 31). It will be shown below that arsenious oxide can be converted quantitatively into arsenic acid with comparative ease. This makes it possible to employ the same substance as a primary standard both in alkalimetry and in oxidimetry. A suitable procedure has been worked out for the standardisation of an alkali solution starting from arsenious oxide, and the titre so found has been compared with that found for the same solution using three other methods of standardisation of known accuracy.

Some Characteristics of Arsenious Oxide Desirable in a Primary Standard.—Arsenious oxide may be purchased commercially at a low price already in a high state of purity. It may readily be purified further both by recrystallisation if necessary and by sublimation. The material used in our work was merely sublimed once, involving an astonishingly small amount of labour in view of the accuracy of the results obtained. White arsenic is not a hydrated substance and can readily be dried by heating, the vapour pressure of the octahedral variety being at 200° and 240° respectively, 0.6 and 6.0 mm. of mercury, while its melting-point is 251° (Welch and Duschak, Bureau Mines, 1915, *Technical Paper* 81). The arsenic acid into which it is converted by oxidation is quickly and largely soluble in water (Menzies and Potter, *loc. cit.*), and yields a colourless solution.

Synthesis of a Decinormal Solution of Arsenic Acid.—The manipulation is simple and does not require, for example, the transference of a precipitate, but close attention to details is well repaid in saving of time.

In our work a good commercial quality of arsenious oxide was purified by subliming once. (This was the "Arsenious Acid of Tested Purity" of Eimer and Amend). To do this a 6×1 inch test-tube was drawn down to one-fourth of its bore at a point a couple of inches from the closed end, and the end pocket so formed was charged with white arsenic. The tube was clamped horizontally, suitably protected by asbestos paper above, and set aside to heat over but not in contact with two lowered Bunsen flames. The sublimate was removed by cutting the tube at the constriction, dried by heating, and bottled hot.

To prepare 500 cc. of 0.1/N solution a quantity of about 2.47 grms. of the powder is weighed out accurately in a 75 cc. conical flask. This is then treated with 5 cc. of chloride-free concentrated nitric acid, followed by 5 cc. of water (the nitric acid is added first, as it wets the powder more effectively than does water) and warmed, at first gently, then more boldly, loss by spattering being prevented by a truncated calcium chloride tube (*cf.* Gooch and Browning, *Am. Journ. Sci.*, [3] xxix., 197). When solution is complete the further addition from a pipette of 5 cc. of concentrated nitric acid serves to wash the calcium chloride tube, which is now removed, and is necessary also to ensure complete oxidation. The solution is then taken to dryness to expel nitric acid. This part of the treatment is vastly expedited by blowing cotton-filtered, ammonia-free air from a small glass jet obliquely on the surface of the liquid, so as to cause rotation of the flask contents. The blower jet is clamped so that its twisted nozzle is close to the liquid surface, while the flask itself is clamped a couple of inches above a heated concave empty sandbath tray and screened from draughts by a

glass cylinder, consisting of a bottomless beaker. It was found that a thermometer whose bulb was placed alongside the bottom of the flask could register a temperature of 180 to 200° without any symptoms of ebullition appearing in the flask.

The dry white residue obtained in this manner still contains nitric acid that is not removable by heating at 230° for many hours. This nitric acid, possibly in solid solution (*cf.* Menzies and Potter, *loc. cit.*), makes its presence evident not only by causing too high acidity but also by responding to the nitron test (Busch, *Ber.*, 1905, xxxviii., 861). The application of this test showed that the nitric acid can be removed for analytical purposes by redissolving the residue in water and taking to dryness again twice. For this purpose, after the first evaporation to dryness with nitric acid the flask is allowed to cool, the residue is covered with distilled water, and the flask then reheated as before. The residue soon dissolves and the air-current evaporates the water again in a few minutes. This treatment with water is repeated, and it only remains to dissolve the residue and to dilute to the required weight or volume of solution.

The Process of Titration.—This has been described and discussed elsewhere (see Menzies and Potter, *loc. cit.*) but may be again outlined for convenience. To a measured quantity of perhaps 30 or 40 cc. of the 0.1/N acid solution are added the phenolphthalein indicator and 3 or 4 cc. of saturated barium chloride solution, a quantity which is largely in excess of that required to form the permanent precipitate mentioned below. The alkali is then run in until the amorphous white precipitate formed locally becomes rather slow in redissolving, which occurs when about one-half of the required alkali has been added. At this stage the titration is interrupted and the vessel scratched beneath the surface of the clear liquid if necessary to induce the formation of the very characteristic lustrous silky crystalline precipitate of BaHAsO_4 , with respect to which the solution is supersaturated. After stirring for a minute to remove this supersaturation the titration is completed in the usual manner. Should the vessel in which the titration is performed have been used for this type of titration already and merely rinsed with water then the minute crystals of BaHAsO_4 remaining on the walls serve to inoculate their supersaturated solution and thus obviate any necessity for scratching. The entire proceeding is perfectly simple if only it be understood by the operator.

Comparison of Titre of Alkali as Standardised by this and by Other Methods.—The analytical details are tedious, as is their narration, which may therefore be curtailed. Weight burettes were employed throughout, and quantities of 30 to 40 grms. of solution were used in the analyses. As indicator 1 cc. of 0.1 per cent phenolphthalein was employed and a 7 per cent transformation aimed at (*cf.* A. A. Noyes, *Journ. Chem. Am. Soc.*, 1910, xxxii., 857). In making the corrections to vacuum the densities of arsenious oxide and of benzoic acid were taken as 3.6 and 1.1 respectively. Carbonate-free sodium hydroxide containing barium hydroxide was employed as alkali and the solutions were kept free from carbonic acid.

(I.). The titre of the alkali was determined against suitably dried (this drying requires care; *cf.* Weaver, *Ibid.*, 1913, xxxv., 1309) benzoic acid (purchased from the Bureau of Standards) by the method described by Morey (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1027). To obtain a satisfactory colour change of the indicator it was found necessary to distil the laboratory alcohol over lime. 0.1/N factor for the alkali found in five determinations was:—1.0037, 1.0037, 1.0040, 1.0045, 1.0041; average, 1.0040.

(II.). Hydrochloric acid of known concentration was prepared by the distillation method of Hulett and Bonner (*Journ. Am. Chem. Soc.*, 1909, xxxi., 390). The 0.1/N factor of this acid was thus synthetically 1.0028.

(III.). The chloride in this acid was estimated gravimetrically, following as closely as possible the procedure

of Morey (*loc. cit.*) in order to obtain results comparable with his. The 0.1/N factor of the acid obtained in four estimations was:—1.0028, 1.0030, 1.0034, 1.0020; average, 1.0026.

The titre of the alkali was now determined against this acid. Using 1.0026 as factor for the acid six titrations gave, as 0.1/N factor for the alkali:—1.0042, 1.0035, 1.0038, 1.0039, 1.0036, 1.0035; average, 1.0037. Using an acid factor of 1.0028 this average would become 1.0039.

(IV.). Five different solutions of arsenic acid were synthesised by the method described, and each of these two titrations were made against the alkali, yielding the following figures for its 0.1/N factor:—(1) 1.0039, 1.0045; (2) 1.0031, 1.0030; (3) 1.0037, 1.0033; (4) 1.0039; 1.0037; (5) 1.0035, 1.0033; average, 1.0036.

The results of standardising the alkali by these various methods may be exhibited most clearly in tabular form:—

Method.	0.1/N alkali factor.
I. Benzoic acid	1.0040
II. Hydrochloric acid, factor from constant boiling pressure	1.0039
III. Hydrochloric acid, factor from AgCl determination	1.0037
IV. Arsenic acid	1.0036

Summary.

It has been pointed out that arsenious oxide is a desirable substance for use as a primary standard in volumetric analysis, and it has been shown that it may be employed, without too complicated manipulation, for this purpose in alkalimetry.—*Journal of the American Chemical Society*, xxxvii., No. 9.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

PRESIDENTIAL ADDRESS, BY DR. ALEXANDER SCOTT, F.R.S.*

(Continued from p. 228).

THE International Exhibition in Hyde Park, held in 1862, amongst its many benefits was not without an influence for good on chemistry and the Chemical Society. It brought many foreign Members into personal contact with the Society to which they had been elected for their pre-eminence in the advancement of our science. It likewise brought about the delivery of lectures in their own language on "Vapour Densities," by St. Claire Deville, on May 15, and by Wurtz on June 5, on "Oxide of Ethylene considered as a link between mineral and organic chemistry."

In 1862 appeared the first volume of what was termed the "New Series" of our *Journal*, which was published in monthly numbers, as now. For many years past the numbering of the volumes has been that which reckons Volume I. of the *Quarterly Journal* as the true starting-point of our regular publications, those for the present year being volumes CIX. and CX., because in each year since 1876 two volumes have been published, of which since 1878 one is *Transactions*—that is, papers presented originally to us for publication—and the other abstracts of work done elsewhere throughout the world.

The lectures delivered by our two French *confrères* had an important effect on our Society beyond even what Hofmann eloquently voiced in the following words:—"In establishing once for ever these international chemical discourses at its meetings the Chemical Society has loudly proclaimed the cosmopolitan character of science, and

* Delivered at the Ordinary Scientific Meeting, April 6, 1916.

that henceforth it will look upon the several nations engaged in scientific pursuits as upon so many federal States of a great Republic united by love of science and pledged by contributions to a common treasury as it were to uphold its cause and raise its dignity." The commencement of lectures so successfully made in this way by distinguished foreigners undoubtedly directed the ideas of the Council and those who desired to perpetuate in a fitting manner the name of one who for his personal gifts as well as for the great extension of chemistry and physics has left his impress on science for all time. Although one of the original Fellows, he could never be induced to become the President of the Society. His name and memory will ever be kept green by the foundation of the Faraday Medal and Lectureship, which was founded in 1869. To the institution of this we owe many notable discourses, which on each occasion, thanks to the kindness of the Managers of the Royal Institution, have been delivered in the same lecture theatre and from the same spot where Faraday had so often held audiences enthralled by the spell of his eloquence, enthusiasm, and perspicacity. It is not generally known that the first six Faraday medals were of palladium, of which precious metal in 1870 Messrs. Johnson and Matthey presented £200 worth for the purpose, and it was hoped that this would be sufficient to make the first ten medals.

Prof. (afterwards Sir Edward) Frankland's Address in 1873 contains much that is of peculiar appositeness at the present time, and shows how slowly methods in education move. After referring to the gratifying increase in the number of original communications made during the year to the Society the President went on to say:—"It must not be for a moment imagined, however, that we have in this important matter taken the position which we undoubtedly ought to occupy as the nation holding the first place in wealth, trade, manufactures, and State revenue. The statistics of experimental discovery show that we are at present very far from the attainment of such a position. I have on a previous occasion expressed the opinion that the chief cause of this deplorable result is the non-recognition of experimental research by our universities. Further inquiries into the conditions under which degrees and honours in experimental science as given here and elsewhere have only served to deepen my conviction that the progress of physics, chemistry, and biology is intimately bound up with the nature of the training prescribed by the governing bodies of universities for students of these sciences, and that until a profound change is made in the awarding of prizes and the granting of degrees in science in this country we shall look in vain for any substantial improvement in the prosecution of experimental investigation."

He then went on to remark on the offering in 1874 of a Fellowship at Trinity College, Cambridge, for proficiency in natural science, in which great weight would be attached to the original dissertations sent in by the candidates, that "such an innovation in the award of Fellowships will be followed with great interest by all who have the progress of scientific discovery at heart. Let us hope that it will inaugurate a new era in the university life of this country."

His words require no apology for my repeating them here, and they indicate how much behind the times the older universities have been in their movements in educational matters. They have undoubtedly done much since 1873, but they have not moved at anything like the rate necessary to enable them to make up the heavy leeway of those days and so take the lead in matters in which it is their function and their duty to direct progress.

In 1874 we entered into possession of the rooms we now occupy, but which in 1892 were rearranged as they now exist. The changes introduced at this later date were the re-seating and rearrangement of the meeting room and attempts to improve its ventilation, which, with some further modifications effected at a very recent date, still leave something to be desired.

The preparation by Mr. Watts of the first volume of the *Collective Indexes* is recorded this year, and covers the period 1841-1872.

In the following year a careful discussion of the financial position of the Society is given, and the growth of the income was considered to be such as to warrant the hope that the Society would be able to dispense with the aid it received from extraneous sources for the purpose of publishing the abstracts from foreign journals. For some years the British Association had given £100 a year, and Fellows had in some years contributed as much as £250, so that this might be done satisfactorily.

In 1876 the admission fee was raised from £2 to £4, but I am glad to say that the annual subscription remains to-day the same as it was fixed seventy-five years ago for Fellows resident within twenty miles of London, namely, at £2. Long may it continue to do so.

The selling price of the *Journal* was raised to £1 10s., at which price it remained until 1895, when £2 was fixed as its price, and owing to its ever-increasing size and cost last year it was found necessary to raise the price to £3.

The Society never succeeded in possessing a Research Laboratory of its own, such as it desired to do in 1841, owing largely to the numerous laboratories and facilities for research having increased. Proposals by Mr. T. Hyde Hills in 1872 to form a fund for making grants in aid of research came to nothing, until in February, 1876, Dr. G. D. Longstaff stated that he was willing to give £1000 to the Society, to be invested and the interest expended in the promotion of chemical research, provided that another £1000 could be raised and applied to the like purpose. A committee was formed, and set to work with such purpose that a sum of £1042 7s. was collected before the meeting of Council on December 21. This was exclusive of a donation of £1000 from the Worshipful Company of Goldsmiths, and at the next meeting of Council on January 18, 1877, Dr. Longstaff presented the transfer of £1000 North British 4 per cent preference stock in fulfilment of his promise. Other City Companies which assisted the fund were the Drapers' Company, who subscribed 100 guineas a year for three years, and the Clothworkers', the Merchant Taylors', and the Mercers', who each gave donations of 100 guineas.

In its final report in April, 1877, to the Council, the Longstaff Committee, as it was called, reports that less than £100 has been received since the issue of the circular in February (Jubilee vol., p. 204). The circular points out that the first list of subscribers are principally scientific chemists, and that with very few exceptions chemical manufacturers have hitherto abstained from aiding this fund.

The Research Fund within three years of its foundation amounted to more than £4300, and continued to receive donations, so that at the time of the Jubilee celebration its capital amounted to a little short of £6000.

The usefulness of the Library was very greatly increased by the decision of the Council to obtain duplicate sets of the more important serials, so that these might be available for circulation, and this policy, initiated in 1879, has been maintained ever since, and, thanks to the beneficence of the late Sir Henry Roscoe and others, our Library occupies in this respect a unique position.

During Sir Henry Roscoe's Presidency the Faraday Lecture by Helmholtz was delivered. The Society of Chemical Industry was also founded, and a Royal Commission on Technical Instruction was appointed by the Government, of which our President was a member, and in his Address in 1882 gave an account of its work.

A very interesting comparison of the opportunities for instruction in pure and applied chemistry was given by Sir Henry Gilbert when he gave an account of those available when he was a student, and contrasted them with what he had seen not only in this country but also during a visit to Canada and the United States.

In 1885 the *Proceedings* were issued as a separate publication and in a form suitable for the publication of preliminary notices of work and short notes on various

subjects, and contained abstracts of all papers read before the Society.

Sir W. H. Perkin and Dr. Hugo Müller, like many of their predecessors, dealt in forcible terms with the lack of encouragement of research and the absolute necessity of high scientific training for those engaged in scientific industries, and their addresses well repay careful perusal, for no two men were ever so fully entitled and qualified to speak authoritatively on the subject.

It was at the end of Dr. W. J. Russell's first year of office that the Anniversary Meeting was held for the first time in the afternoon, and after the meeting the Fellows dined together, a custom which has been kept up by not an annual but a biennial dinner with few exceptions ever since until the present war, to be resumed again we hope in happier times.

An event of great importance in the history of the Society was the celebration in 1891 of the Jubilee of its foundation, which consisted of an afternoon meeting, when addresses were delivered and delegates received from many learned societies at home and abroad; an evening reception and *soirée* in the Goldsmiths' Hall, where an exhibition of historical and of interesting apparatus and specimens was shown, and finally a dinner on the succeeding evening, attended by the Marquis of Salisbury, then Prime Minister, and other distinguished guests.

During the presidency of Prof. Crum Brown the first of the memorial lectures on the life and work of Jean Servais Stas, from the pen of the late Prof. Mallett, was given, to be followed after a brief interval by one on Hermann Kopp by Sir Edward Thorpe, to whose ready pen and sympathetic treatment we owe so many of the later memorial lectures.

The Faraday Medal was presented to Lord Rayleigh for his work on the discovery of argon at the close of Prof. Armstrong's term of office in 1895, and the meeting was rendered still more memorable by Sir William Ramsay's account of the discovery and preparation of helium from cleveite, Sir William Crookes giving an account of the spectroscopic evidence proving its identity with that of the element in the atmosphere of the sun.

In 1898 the Society entertained to a banquet six of its Past Presidents who had been Fellows of the Society for fifty years—namely, F. A. Abel, E. Frankland, J. H. Gilbert, J. H. Gladstone, W. Odling, A. W. Williamson. The celebration was originally fixed for June 8, and it was confidently hoped that the last survivor of the original members of the Society, Lord Playfair, who was President in 1857–1859, would have been present, but his death on May 30 disappointed all and led to the postponement of the dinner until November 11.

A second celebration of the same kind was held on November 11, 1910, when the following five Past Presidents were invited to be the guests of the Society—namely, W. Crookes, A. G. V. Harcourt, H. Müller, W. Odling, H. E. Roscoe, and of these one had been entertained at the earlier banquet, and happily is still with us.

The advent of the new century was fitly marked by Sir Edward Thorpe giving a most interesting historical account of chemistry from the beginning of the past century up to the foundation of the Society. In 1901 the death of Queen Victoria, whose beneficent reign began a few years before the foundation of our Society, led Sir William Tilden in 1904 to complete, with his well-known skill, the modern history of chemistry by giving a summary of the progress of chemistry during the Victorian era. The Society also owes to Sir William Tilden the initiation of the "Annual Reports on the Progress of Science," of which twelve volumes have now been published. Thanks to the self-sacrificing labours and energy of those of our Fellows who take part in their preparation, they are justly regarded as the most complete in their way, and are unique both from the promptness with which they are published and the ground they cover.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY
(LONDON SECTION).

Ordinary Meeting, May 1, 1916.

Mr. ARTHUR LING in the Chair.

THE CHAIRMAN announced that as a result of the ballot, the following five new members for the Committee had been nominated, and, subject to the vote of the members, would be elected to serve on the Committee:—Messrs. T. F. Burton, E. Grant Hooper, C. A. Keane, J. W. McDonald, A. Gordon Parker, *vice* Messrs. F. H. Carr, C. A. Hill, R. Lessing, G. W. MacDonald, and T. Tyrer, who retire.

The following papers were read:—

"The Sulphur Impurity in Coal Gas." By FRANK CLOWES, D.Sc., F.I.C.

The removal of sulphur compounds from coal gas, said the author, is a problem of the greatest interest to chemists, but the progress made has been, until recently, slow. Coal itself may contain from 0.5 to 4 per cent of sulphur, present partly in the form of inorganic compounds and partly as organic compounds. Good gas coal should not contain more than 2.5 per cent of sulphur. Fire-clay retorts have now replaced the original iron, and whilst this change has ensured a larger yield of gas, it has caused a higher proportion of sulphur to pass into the gas, and this increase is mainly in organic sulphur compounds, which are difficult of removal. The crude gas from the retorts may contain 1.6 per cent by volume of hydrogen sulphide and 0.03 per cent of carbon bisulphide and other organic sulphur compounds. The removal of the hydrogen sulphide is effected by passing the gas over hydrated ferric oxide, whilst the organic sulphur compounds are in some works removed by subsequently passing the gas over sulphided lime. This lime, however, does not effect the desired object either certainly or completely, and sulphur amounting to 10 grains per 100 cubic feet may still remain in the gas. The gas-maker also contends that its use causes much nuisance, and is injurious to the health of the workmen. As a rule, the lime purification is only used in those gasworks which are required by law to keep the quantity of sulphur in their gas at about 20 grains per 100 cubic feet. The limits of 17 grains per 100 cubic feet of sulphur in summer and 22 grains in winter, imposed by the Gas Act of 1860, held for London gas until a few years ago. Now, however, the purification of the Metropolitan gas supply depends, as it has long done in some other large centres, upon the use of oxide of iron, and lime is not used.

In 1904 the Metropolitan gas companies asked to be relieved of the limitation prescribed for the sulphur impurity, basing their request mainly on the uncertainty in working the lime process and the other reasons already stated. It was also suggested that the consumers in districts where this process was not carried out made no complaint, and, further, that the introduction of the mantle-burner led to a considerable reduction in the amount of gas consumed for illuminating purposes, and to a corresponding diminution of the quantity of oxidised sulphur compounds introduced into the atmosphere of dwelling-houses. The Board of Trade appointed a Committee, consisting of independent scientific men and representatives of the gas industry, who recommended that the test for hydrogen sulphide should be carried out by exposing a wet lead paper at intervals to the gas for three minutes, instead of exposing a dry lead paper continuously for at least fifteen hours, which had been the practice. They also recommended the discontinuance of the lime process, it being assumed that the absence of complaint by gas consumers in districts where lime purification was not used was evidence that the additional sulphur in these gas supplies was not prejudicial. But Dr. Haldane found that gas not purified by lime gave rise to sulphur combustion products prejudicial to comfort, and even in some cases to health, whilst they had no disinfectant value. It

was also proved by Dr. Gordon Parker that such gas when burned exerted a most destructive effect on leather and fabrics generally.

The author pointed out that it can scarcely be imagined that so destructive an agent as the products of the combustion of sulphur in gas could be allowed to be introduced into the air of a dwelling-house, reliance being placed on its removal by ventilation or other means, which could not be effected before some damage was done. It was stated in evidence that the plaster and freshly lime-washed surfaces of the ceilings and walls of rooms would remove these oxidised sulphur compounds, but the fact was ignored that the surfaces presented to the air of a room are usually protected by the use of size, or by paint or varnish. The sulphur difficulty has recently been met by the work of Dr. Charles Carpenter, who has perfected a simple economical and successful process of reducing the sulphur impurity in coal gas without the use of lime. It seemed probable that the incitement to perfect this new process arose largely from the statements made before the Board of Trade Committee, and from the decision at which that Committee arrived.

Dr. Carpenter's process consists in passing the gas over fire-clay surfaces impregnated with reduced nickel, at a temperature of about 450° F., and subsequently removing the hydrogen sulphide thus produced by means of ferric oxide. It has now been working continuously and economically in four of the largest works of one of the large Metropolitan gas companies for eighteen months with perfect success, and has given no cause for trouble or delay. Dr. Carpenter expresses the opinion that the future policy of the gas industry would consist in supplying gas in the state of the greatest possible purity.

DISCUSSION.

Dr. C. CARPENTER (President of the Society) complimented Prof. Clowes on the interesting history he had given—of what for so many years had been called in London "The Sulphur Question." It was true that many years had been spent dating back to the time when Dr. Brand was the Secretary of the Royal Commission, on the problem of sulphur purification, and the lime process seemed to be an insoluble one. The catalytic process in practically all its details had been suggested and foretold almost thirty years ago; e.g., by Sir W. Stevens. In the past there had been much delay owing to the fact that chemists and engineers did not collaborate as they might have done, but one of the best examples of men who had so collaborated was Mr. Harry Jones, who might be described as the doyen of the gas industry. He was the first to apply himself to the problem of the extraction and recovery of bisulphide of carbon from gas.

Mr. HARRY JONES said that in achieving the feat with which he had been accredited by Dr. Carpenter he had had the help of Mr. Lester Greville, who was an assistant of Dr. Keats at the County Council. Dr. Keats had pointed out in evidence that the gas companies as soon as they got the lime in a condition to be really useful for taking the sulphur out immediately carted it across a street or on to a barge, and made an outrageous nuisance of it. He had told them that a wheel-barrow of lime in a proper condition would eliminate all the sulphur that was necessary, whereas they used tons of it, and threw it away just as it became useful. In all gas there was a large amount of carbonic acid, which would replace the sulphur in the lime when passed through it. Hence it was that when carbonic acid was present the gas might contain more sulphuretted hydrogen after passing through sulphided lime than before. He urged that the sulphur recovered from gas purification was better adapted for the production of sulphuric acid as it did not contain arsenic. His experience had proved that the old-fashioned leather was not affected by burning coal gas.

Mr. W. A. BUTTERFIELD said that it was important to bear in mind that the sulphur compounds about which the author had been speaking represented only 1/18th to

1/20th of the sulphur initially present in the crude gas. The introduction of the incandescent mantle had reduced the amount of sulphur burned in illuminating a room to about 1/10th of what it was before. Therefore legislation that a company should keep the sulphur compounds in the gas down to a minimum which was necessary before the introduction of the incandescent mantle became ridiculous at the present time. It was a matter of the proportion of sulphur dioxide in the air of the room which caused the effects shown in the samples exhibited by Dr. Gordon Parker.

Dr. S. RIDEAL said that prior to 1904 he had visited several countries in connection with the sulphur question, and was astonished to find in Brussels, Berlin, Vienna, and in Paris that the sulphur question had not been before them in the way it had been in England for the last forty or fifty years. It seemed unknown, and he could not find any lime purifiers at all. Yet in this country they had had so many fights for a great number of years trying to remove only a small percentage of the residual sulphur in gas. He believed Dr. Parker's experiments were illustrations of how not to make leather stand in an ordinary town atmosphere. He (the speaker) had exposed samples of metal outside workmen's dwellings in Old Kent Road, some in one room in which the gas had been purified by means of lime and in another room in which the gas had not been purified, and some outside. The effect upon the metals was more pronounced in the outside air than in the rooms. The blackening of metals was due to sulphuretted hydrogen produced by the incomplete combustion of coal in grates in towns, and from manure heaps and decaying vegetables in country places. The sulphuretted hydrogen had, however, always been removed by gas companies, and that could not have been an offender in the past or in the present.

The CHAIRMAN said that he had noticed when lime purification was discontinued, the amount of copper sulphate formed by the impinging of gas flames on the copper vessels in his laboratory had very much augmented. A considerable amount of this salt was swept from beneath his copper vessels every week. He was sure that the products of the incomplete combustion of coal gas, e.g., when a flame impinged upon a metal surface, such as an inverted incandescent mantle or the bottom of a copper vessel, contained sulphuretted hydrogen. He had ample proof in his own house in the summer time when there were no coal fires that silver plate was blackened by burning coal gas in the room. They were all aware of the presence of arsenic in sulphuric acid made from pyrites, but arsenic was also present in sulphuric acid made from recovered sulphur.

Prof. CLOWES having briefly replied, a vote of thanks was passed to him.

"Evaporation of Naphthalene in Dry and in Moist Coal Gas." By J. S. G. THOMAS.

Previous work on the evaporation of naphthalene in dry coal gas, by Allen (*Journ. Chem. Soc.*, 1900, lxxvii., 400) and Schlumberger (*Journ. fur Gasbeleuch.*, 1912, p. 1257), yielded results in practical agreement over the range from 30° to 50° C., whereas over the important range of temperature from 0° to 30° C. the values obtained by Allen are considerably higher than those obtained by Schlumberger. As a preliminary to an investigation into the effect of various vapours upon the saturation naphthalene content of coal gas which the author was requested to undertake by Dr. Charles Carpenter, the saturation naphthalene content of dry coal gas has been determined by the author, and the effect of water-vapour upon the saturation content also investigated. Throughout the range from 0° to 60° C., the author obtains results in practical agreement with the results of Schlumberger in the case of dry coal gas. In the case of moist coal gas between 0° and 30° C. he finds that the saturation vapour pressure of naphthalene is less than that in dry coal gas, the ratio of the saturation naphthalene content of moist coal gas to the saturation

tion naphthalene content of dry coal gas approaching continuously more nearly to a ratio of equality as the temperature is raised from 0° to 30° C. Above 30° C. the saturation naphthalene content of moist gas is found to be slightly greater than the saturation naphthalene content of dry gas.

The author seeks to explain these results on the basis of the condensation of a skin of water upon the naphthalene in the case of moist gas, and theoretical considerations were advanced showing that this theory is in qualitative agreement with the experimental results.

DISCUSSION.

The CHAIRMAN said that they must all have been struck with the fact of how much they were indebted to the President and his staff for the most valuable work they were carrying on, as shown by the important paper they had just heard.

Dr. C. CARPENTER explained the practical utility of the work which Mr. Thomas had carried out. They had two difficulties to contend with in regard to gas supply; one was the sulphur content and the other the naphthalene content, which latter was so apt to cause trouble especially in winter by stopping up the pipes. Basing their belief on the work of Allen, they came to the conclusion that if the naphthalene content could be cut down to something like 12 grains per 100 cubic feet they would be absolutely immune from trouble. Under these circumstances, however, they found that the trouble increased. When Mr. Thomas looked into the problem and made his most valuable and interesting experiments, it proved that what they had actually found in practice had a true foundation, that the amount of naphthalene carried was something like half or less than the figure they were led to expect by Allen.

Mr. THOMAS, in reply, thanked Dr. Carpenter for his very kind remarks, and said that throughout the whole of the investigation Dr. Carpenter had inspired the work with his continued interest and suggestions, and he could only tell the members of the Society how much any value the work might have was due to Dr. Carpenter's inspiration.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 3, 1916.

Mr. GEORGE EMBREY, President, in the Chair.

MR. Maurice S. Salamon was elected a member of the Society.

The following papers were read:—

"Salvarsan and Neo-salvarsan, Excretion and Secretion of." By JOHN WEBSTER, F.I.C.

Results of analyses, showing the relative amounts of arsenic found in the various organs after injections of salvarsan and neo-salvarsan, were shown, special attention being drawn to the relatively very high proportion of arsenic present in the kidneys in one case in which post-mortem examination had shown that nephritis was present.

Various analyses of urine were given showing the variability of the rate of excretion.

Analyses of human milk from two cases of salvarsan treatment were referred to. These analyses showed that after a dose, or repeated doses, of salvarsan, the milk of a lactating woman is entirely, or almost entirely, free from arsenic (a minute trace of arsenic being found in one specimen only). Any beneficial results to the syphilitic child fed on such milk cannot be due to the presence of salvarsan or other compound of arsenic in the milk of the mother.

"Microscopical Methods." By Prof. GREENISH, F.I.C. The author, confining his remarks to the treatment of vegetable powders, explained in some detail the methods

that he had found satisfactory and was in the habit of employing for examining, identifying, and determining the purity of a simple powder, and for ascertaining the composition of a mixed powder.

He explained the advantages that may be derived from concentrating certain tissues by the removal of other constituents by suitable means, and described a method for determining whether a powder had been prepared from worm eaten material.

He dealt finally with a method for the treatment of faeces in order to separate the undigested vegetable and animal matter for the detection of the tissues of ingested drugs.

NOTICES OF BOOKS.

The Practical Principles of Plain Photo-micrography. By GEORGE WEST. Dundee: Campbell, Sons, and Co. 1916. Pp. x.+145. Price 4s. 6d. net.

THIS is an exceedingly useful book, and both experienced microscopists and beginners in the art will find it well worth their while to get a copy and study it thoroughly. The author has had an extensive experience in photo-micrography, and his conclusions will well repay careful consideration. The book abounds in practical suggestions, especially relating to details which escape mention in more formal and advanced works, and the student who hopes to undertake microscopical research work will be greatly aided in the early part of his career by spending some time in improving his technique with the help of this book. A full account is given of the arrangement with a landscape camera finally adopted by the author after many experiments, and adaptations and details of the cost are included, with lists of photographic necessities and notes upon their use. The book is embellished with some really beautiful plates illustrating various subjects, descriptions of which are provided.

A Study of the Quality of Platinum Ware. No. 254, Scientific Papers of the Bureau of Standards. By GEORGE K. BURGESS and P. D. SALE. Washington: Government Printing Office. 1915.

In this bulletin a series of experiments on the loss of weight of platinum crucibles of various qualities on continued heating is described. The authors find that for the determination of the purity of platinum ware the most exact method is the measurement of the temperature coefficient of electrical resistance, which is known for pure platinum, and which diminishes with the addition of anything to the metal. Full details are given of the method of carrying out the determination, and the results of the examination of fourteen crucibles of different degrees of purity are discussed. It was found that the presence of iridium causes a greater loss of weight than that of rhodium, while iron appears to lessen the loss, but its presence is objectionable owing to the formation of soluble oxide. In specifications of the highest grade crucibles it is suggested that it should be required that rhodium should be substituted for 5 per cent of iridium, and that iron should be eliminated.

Representative Procedures in Quantitative Chemical Analysis. By FRANK AUSTIN GOOCH. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1916. Pp. x.+262. Price 8s. 6d. net.

THIS book provides a very suitable course of quantitative chemical analysis for older students who are prepared to devote a good deal of time to the thorough study of the subject. Much stress is laid upon the need for a good knowledge of theoretical principles as a basis for satisfactory experimental work, and references are given to a few easily accessible books for further reading. The first

section, on gravimetric work, is preceded by a discussion of methods of weighing and measuring, in which full details are given for testing the sensitiveness of the balance and the accuracy of the weights. The different processes employed gravimetrically are classified according to the essential principles involved in them, and directions are given for typical processes, including electrolytic work. In every case discussions of the theory of the methods precede the directions for the performance of the experimental work, and the latter are very full and complete, such details as the contamination of precipitated barium sulphate being thoroughly discussed. In the volumetric part special attention is paid to iodometric methods, and gasometric processes are included, *i.e.*, those in which the gases involved in a reaction are estimated, as well as some colorimetric processes. A section on systematic analysis is given and a few methods of indirect analysis are also described.

MISCELLANEOUS.

The "van't Hoff Fund" for the Endowment of Investigators in the Field of Pure and Applied Chemistry.—In agreement with the regulations of the "van't Hoff Fund," founded on June 28, 1913, persons interested are informed herewith of the following particulars:—The foundation, whose residence is Amsterdam, and of which the supervision is vested in the Royal Academy of Sciences there, is appropriated to give from the rents of the fund every year before March 1, endowments to investigators in the field of pure and applied chemistry, who will have applied for such an endowment before November 1 preceding the above mentioned date, to the Committee charged with considering the applications and awarding the grants. This Committee is constituted as follows:—A. F. Holleman, President; S. Hoogewerf; A. Smits; E. H. Büchner, Secretary. If desirable, this Committee may appoint still other members for one year only, to co-operate in judging of the applications made. The names of persons to whom a grant is allowed will be published. The grantees are requested to send to the Committee some copies of the papers relating to the results of their work; but for the rest they are at liberty to choose the manner of publication, as well as the journal, in which they like to publish their results, if only they mention the fact that the research was made with an endowment from the "van't Hoff Fund." The amount available over 1917 is about £200. Applications should be sent, registered by post, to Het bestuur Koninklijke Akademie van Wetenschappen, bestemd voor de Commissie van het "van't Hoff Fonds," Trippenhuis, Kloveniersburgwal, te Amsterdam—with a detailed account of the proposed use of the grant and of the reasons on which the candidates ground their claim. They must be received before November 1, 1916.—In the name of the Committee of the "van't Hoff Fund," A. F. HOLLEMAN, President; E. H. BÜCHNER, Secretary. Amsterdam, May, 1916.

MEETINGS FOR THE WEEK.

- MONDAY, 22nd.—Royal Society of Arts, 4.30. (Cantor Lecture). "Vibrations, Waves, and Resonance," by J. Erskine-Murray.
- TUESDAY, 23rd.—Royal Institution, 3. "Unconscious Nerves Their Functions in External Life," by Prof. Charles S. Sherrington.
- WEDNESDAY, 24th.—Royal Society of Arts, 4.30. "Zinc, its Production and Industrial Applications," by J. C. Moulden.
- THURSDAY, 25th.—Royal Institution, 3. "The Beginnings of the Orchestra and its Instrumental Combinations," by Sir Alexander Mackenzie.
- Royal Society, 4.30. (The Bakerian Lecture) X-Rays and the Theory of Radiation," by Prof. G. C. Barkla, F.R.S.
- FRIDAY, 26th.—Royal Institution, 5.30. "X-Rays," by Prof. C. G. Barkla.
- SATURDAY, 27th.—Royal Institution, 3. "The Finance of the Great War—How We Stand To-day, and What Lies Ahead," by Prof. H. S. Foxwell

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The Owners of BRITISH PATENT No. 28,108 of 1906, entitled "Improved Process or Method of Utilising Nitrogen contained in Distillers' Washes," are desirous of disposing of the Patent or entering into working arrangements, under Licence or otherwise, with firms likely to be interested in the same. A copy of the Patent Specification and full particulars can be obtained from, and offers made (for transmission to the Owners) to MARKS and CLERK, 57 & 58, Lincoln's Inn Fields, London, W.C.

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THE CHEMICAL NEWS.

VOL. CXIII., No. 2948.

A SIMPLE METHOD FOR VAPOUR-DENSITY DETERMINATIONS.

(PART XV.).

By PHILIP BLACKMAN.

(Continued from p. 127).

IN all forms of the apparatus hitherto described the length of the manometer is determined by the extent of the heating apparatus, and in the most advantageous cases cannot be very great. It is, however, quite possible to have the manometer *outside* the heating apparatus (Fig. 6); then it may be made of any length (the longer the better), and an ordinary large beaker may be used as a heating vessel. Several cc. of mercury must be left over in the bulb to ensure that at t_2° the capillary bore from the bulb to well outside the heating vessel is filled with mercury (otherwise if the bore of the capillary from the neck of the bulb to

(2) The final total pressure at t_2° = that in the manometer at t_3° =

$$\frac{\psi a L_c (273 + t_3)}{a l (273 + t_1)} = \frac{\psi L_c (273 + t_3)}{l (273 + t_1)}$$

(3) The pressure of the air only in the bulb at

$$t_2^\circ = \psi (273 + t_2) / (273 + t_1).$$

(4) The volume of the vapour at 0° C. and 760 mm. pressure is 11160 w/d (assuming that 1 grm. of hydrogen at 0° C. and 760 mm. pressure occupies 11160 cc.), and at t_2 the volume is still V , and therefore the pressure is—

$$\frac{11160 \times 760 w (273 + t_2)}{273 d V}$$

But (3) + (4) = (2), from which on simplification—

$$d = \frac{31068 w l L_c (273 + t_1) (273 + t_2)}{\rho L V [L_c (273 + t_3) - l (273 + t_2)]}$$

(It will be seen that if $t_3 = t_2$, i.e., if the *whole* apparatus be heated at t_2° C., the formula becomes that given in the first part of the paper).

At fairly high temperatures p must be written $\rho - q$, where q is the correct vapour pressure of mercury.

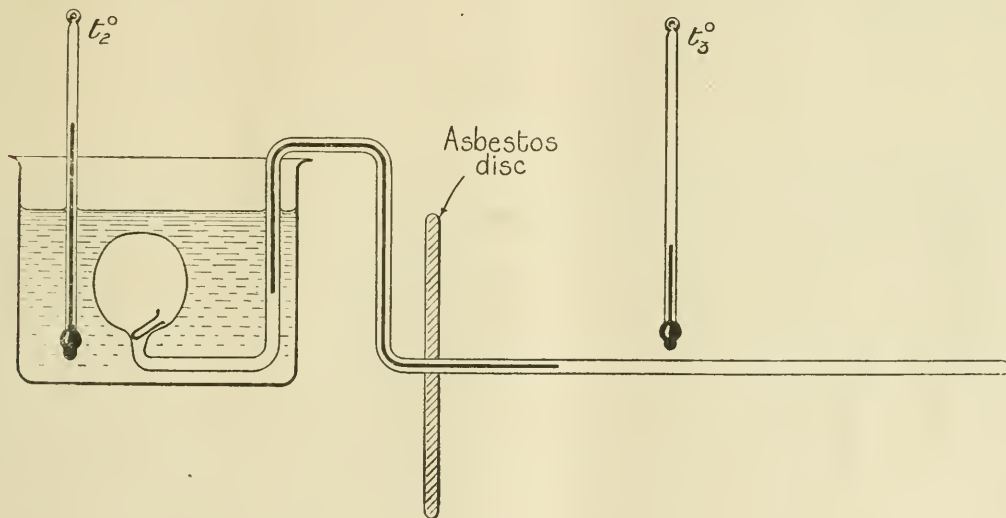


FIG 6

anywhere without the heating vessel be empty the vaporised substance will naturally tend to condense into the outside cooler region, and if the mercury thread extends from the neck of the bulb not well outside the heating vessel the air in the manometer will not be throughout at one temperature, viz., the room temperature), and also on account of the necessity of having this excess of mercury within the bulb substance whose vapours react upon mercury cannot be experimented upon with this form of apparatus, but if the apparatus have a very long spirally-twisted neck (Fig. 7) and the mercury thread be so arranged that it begins about a quarter to half of the length of the neck from the bulb then the apparatus can be so used.

The necessary calculating formula for the vapour density with this apparatus is derived as follows:—

Let t_3° C. be the external temperature when the reading l has been made, d = the vapour density, a = the area of the cross section of the capillary bore.

(1) The initial internal pressure t_1°
= $\rho a L / a L_c = \rho L / L_c = \psi$.

Results.

$\text{CH}_3\text{CO.CH}_3$.— $\rho = 757$ mm.; $L = 847$ mm.; $L_c = 858$ mm.; $V = 257.3$ cc.; $w = 0.5116$ grm.; $l = 383$ mm.; $t_1 = 17^\circ$ C.; $t_2 = 100^\circ$ C.; $t_3 = 18.5^\circ$ C.; vapour density (determined) = 29.2 (theoretical, 29.0).

C_6H_6 (benzene).— $\rho = 763$ mm.; $L = 819$ mm.; $L_c = 832$ mm.; $V = 246.2$ cc.; $w = 0.7620$ grm.; $l = 329$ mm.; $t_1 = 19.5^\circ$ C.; $t_2 = 100^\circ$ C.; $t_3 = 16.0^\circ$ C.; vapour density (determined) = 38.6 (theoretical, 39.0).

If this form of apparatus be used in the quantitative analysis of a binary mixture it can easily be shown that the formula for calculating the percentage weights (w_1 and $100 - w_1$) is—

$$d_2 w_1 + d_1 (100 - w_1) = \frac{100 d_1 d_2 \rho L V [L_c (273 + t_3) - l (273 + t_2)]}{31068 w l L_c (273 + t_1) (273 + t_2)}$$

Results.

CH_3OH and $(\text{CH}_3\text{CH}_2)_2\text{O}$ (w_1 , $100 - w_1$, and d_1 , d_2 respectively).— $\rho = 759$ mm.; $L = 801$ mm.; $L_c =$

812 mm.; $V = 240.8$ cc.; $w = 0.5472$ gm.; $l = 341$ mm.; $t_1 = 18.5^\circ$ C.; $t_2 = 100^\circ$ C.; $t_3 = 18^\circ$ C. Found— $w_1 = 11.8$ per cent, $100 - w_1 = 88.2$ per cent. Actual weights— 0.0646 gm., 0.4826 gm. and per cent = 11.8 and 88.2 respectively. ($d_1 = 16.0$; $d_2 = 37.0$).

$t_3 = 19.0^\circ$ C. Found— $w_1 = 50$ per cent, $100 - w_1 = 50$ per cent. Actual weights— 0.2505 gm., 0.2503 gm., and per cent = 50 and 50 respectively.

(NOTE.—To avoid as much as possible the expenditure of much glass tubing in the carrying out of the large

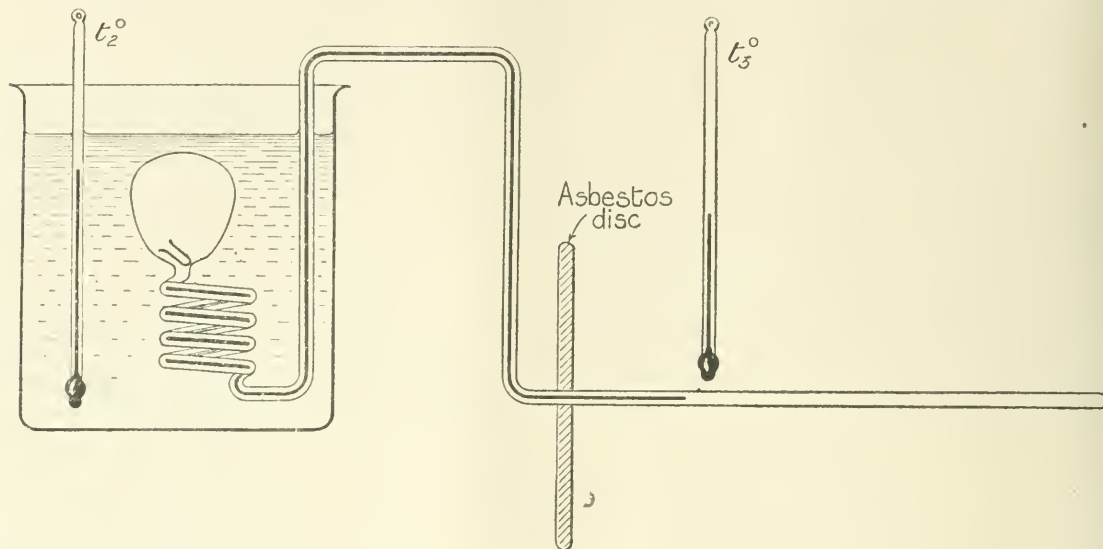


FIG. 7.

$C_2H_5.OH$ and CCl_4 (w_1 , $100 - w_1$, and d_1 , d_2 respectively).— $d_1 = 23.0$; $d_2 = 76.9$; $\rho = 767$ mm.; $L = 788$ mm.; $L_c = 799$ mm.; $V = 235.4$ cc.; $w = 0.5008$ gm.; $l = 363$ mm.; $t_1 = 20.0^\circ$ C.; $t_2 = 100^\circ$ C.;

number of experiments, several devices were resorted to in order to use over and over again the same tubes; thus, the bulb at one end had a tube several inches in length, and just wide enough to admit the weighing tube (w), but which on cutting off the end to determine the volume V did not greatly reduce the bulb's capacity, and when this was entirely cut off after a number of determinations another similar tube was fused on; again, the end of the capillary tube was generally cut off only after every third or fourth experiment for cleaning purposes, the cleaning and drying being carried out as often as possible by aid of a long thin drawn-out "re-fill" (Fig. 8), and when too short was cut off altogether and another affixed. Also, the substance to be experimented on was enclosed (sealed) in a previously weighed very thin drawn-out glass tube, and thus weighed introduced into the bulb with a heavy piece of glass-rod, and after the bulb was sealed and L_c was measured this extremely fragile tube was easily broken—to liberate the enclosed body—by gently shaking the glass-rod against it. From the illustrations one might think that only long bulbs were used; occasionally round bulbs were employed, made from ordinary small distilling flasks).

Hackney Technical Institute, London, N.E.



FIG.

Russian Dyemaking Scheme.—A Petrograd report states that the scheme for establishing coal-tar colour works in Russia has not been abandoned. A project is under discussion which is said to have the support of the leading dyestuff consumers in the country, and it is thought to have very good prospects of success. The proposed capital of the concern is 5,000,000 dols., the whole of which is to be provided by home consumers. It is stated that the seven largest calico-printing companies in Russia (including the Baranoff Company, the well-known printer and Turkey-red dyers, and the E. Zündel Company Moscow), representing an aggregate capital of over 25,000,000 dols., have together promised about 2,200,000 dols. toward the new undertaking. It is proposed to erect tar-distilling plants and manufacture right from the raw product.—*Chemical Engineer*, xxi., No. 3.

THE PROPERTIES OF SOLID SOLUTIONS OF METALS AND OF INTER-METALLIC COMPOUNDS.*

By F. C. THOMPSON, M.Met., B.Sc.,
Demonstrator in Metallography in the University of Sheffield.

It is a profoundly interesting fact that almost without exception the alloys which are of industrial utility consist of one or more solid solutions. The brasses, almost the whole of the bronzes, all the copper-zinc-nickel alloys ("nickel-silvers") which find practical application, most of the coinage, and that most important branch of light aluminium alloy for aeroplane and motor-car construction, all consist entirely, or almost so, of such a constituent. Even in the case of the steels the all-important property of hardening is due to the formation, and the more or less complete preservation on quenching, of a solid solution. The nickel and other special steels also which find so great employment in engineering construction owe their special properties, in part at least, to the improvement in the ferrite arising from the presence of the alloying metal in solid solution. The practical explanation of the overwhelming superiority of those alloys which consist of solid solutions when compared with the pure metals is found in the remarkable "toughness," or combination of strength and ductility, which is their dominating characteristic.

Concerning the hardness bestowed on a metal by solution in it of another much has been written. Even now, however, the real explanation of the facts is by no means fully understood, so that in view of the supreme practical importance of the question it seems advisable to pursue it further.

In addition to the hardness of the alloys under consideration, another specially characteristic property is their high electrical resistance. Now, hardness and high electrical resistance are also characteristic of metals in the hard-worked state, and in general the physical properties of hard-worked metals and of metallic solid solutions are so much alike as to lead almost inevitably to the conclusion that some common cause is operating in each. In comparative tensile tests of a metal in the annealed and in the totally work-hardened states, the maximum stress has in the latter case been raised, and the elongation before fracture reduced until it has become inappreciable. These properties find their parallel in the solid solutions. The brass with 46 per cent of zinc has a maximum stress of 30 tons per square inch, that of copper being about 14 tons per square inch, while the elongation has fallen to under 5 per cent. The parallelism does not end here. It has been pointed out more than once that by cold-rolling the tenacity of a metal may be exactly doubled (Charpy, "Contributions à l'Etude des Alliages," Paris, 1901, p. 1). The tensile strengths of copper and of the copper alloy with 46 per cent of zinc, already given, show the same effect. In the silver-gold alloys—metals which form an uninterrupted series of solid solutions—the maximum sclerometric hardness is almost exactly double that of either pure metal, and similarly almost exactly equal to that of, for instance, silver which has been hammered dead hard.

The results of electrical conductivity measurements point in the same direction. The addition of nickel to the copper-zinc alloys raises the specific resistance just as cold-rolling does, and to such an extent also that the further influence of deformation in the cold becomes negligible. A "nickel-silver" with 28 per cent of nickel, 12 per cent zinc, and 60 per cent copper has, when in the hard-worked state, a specific resistance of 41.5 microhms per cc., and after full annealing at 800° C. a resistance of 41.3.

The specific volume of a metal is influenced to only a very small extent by cold work. It is therefore of interest that, in the simplest cases, solid solutions in metals are

formed from the components without change of volume, the specific volume being a strictly lineal function of the concentration.

Considering therefore the really remarkable parallelism between the properties of a metal in the "écroui" condition and when in solid solution with another metal, the assumption is perfectly justifiable that distortion of the crystalline matter is equally present in the latter case and in the former. From whence, then, does this internal strain to be assumed in the solid solutions arise?

It is now a thoroughly established fact that the atoms of any crystal are arranged in space with perfect regularity. Taking in each atom a similar point, the space lattice on which the crystal is built is obtained. The unit of this lattice is therefore, in the case of the majority of metals, a cube whose side is $\sqrt[3]{v}$, where v is the atomic volume.

That metallic solid solutions are truly crystalline needs no labouring; cleavage slipping under stress, beautifully definite etching pits, single and repeated twinning, can point to no other conclusion. In the space lattice of such a solution the lattices of the two or more constituents are regarded as interpenetrating. The conditions may be more easily followed, however, by considering one space lattice only. In the case of an element A to which a second B, which passes into solid solution, is added, the atoms of A in the space lattice are replaced progressively by those of the isomorphous B, and the lattice passes imperceptibly from that of the one pure element to that of the other.

Now, this atomic replacement in the lattice must react on the physical properties. It implies, as Gossner has suggested (see Tutton, "Crystalline Structure and Chemical Constitution," 1910, p. 128), an attempt at the equalisation of the atomic volumes of the components in the solution, and if the atom of A occupies a greater volume than that of B, the replacement must result in an expansion of B and a contraction of A in the act of crystallising together.

The resulting distortion must give rise to elastic strains, probably of a high order, throughout the whole mass, to which the increased hardness of this class of alloy must be ascribed. The extent of the strain on this theory will depend, among other factors, on the extent of the atomic replacement, and should be greatest when half the atoms have been replaced by others. It is valuable evidence, therefore, in favour of the view propounded that in those series of binary alloys, such as gold-silver or gold-copper, which form an uninterrupted series of solutions the maximum hardness is invariably found when 50 per cent of each component is present.

We may now consider in what way the hardness of an alloy may be expected to vary with composition, if the condition of internal strain which must arise if the conception be true of the equalisation of the atomic volumes of the constituents in such crystalline aggregates be the true cause of the hardening.

If the solution of B and A be very dilute, and if the reaction on the atoms of A be distributed uniformly over all, the change in the volume of each atom will be small. On the other hand, since the atoms of B are few the change in volume in each will be great. The atoms of B therefore are compelled to assume practically the atomic volume of A. But as more of B is added the change of atomic volume, and hence the rate of increase of hardness with concentration, will become less and less. The additions of B already made will have produced a tendency for the mean atomic volume to approach more nearly that of the added metal, so that the increased strain produced by each further addition will become smaller. The theory of the increased hardness here propounded would therefore, in the simplest case where the component metals are completely isomorphous, lead to a curve for the relationship of the hardness of an alloy to composition which rises sharply at each end, as small quantities of each metal are dissolved in each other, and then rises less and less steeply, reaching a flattened maximum with the alloy containing

* A Paper read before the Faraday Society, May 9, 1916.

50 per cent of each metal. The parabolic curve obtained experimentally for such alloys, e.g., gold-silver, fulfils these requirements of the theory absolutely.

It is, however, possible to predict still more closely the type of the hardness-concentration curve of a binary series of alloys of isomorphous metals.

Consider an alloy containing x atomic per cent of an element A whose atomic volume is v_1 dissolved in a metal B the volume of whose atom is v_2 . The tendency to equalise the volumes of the atoms of both A and B will increase that of B (assumed the smaller) and decrease that of A.

Now, since there is no evidence of any marked change in the closeness of the packing of the atoms with alterations of concentration in such solutions, and since the greatest divergence of the specific volume of any of the alloys from that calculated according to a straight line relationship does not exceed 0.2 per cent, it may be assumed that the mean atomic volume of the crystalline solution will be the arithmetical mean, i.e.,—

$$v_m = \frac{xv_1 + (100-x)v_2}{100}$$

Further, the increased strain-energy arising from the stresses set up by the replacement will be the sum of the strain-energies arising from forcing the atoms of A and of B to conform to the mean atomic volume. Now, if the coefficients of cubical expansion are Ka and Kb respectively, the extra internal strain-energy resulting from the solution is:—

$$\begin{aligned} & \frac{1}{2} \cdot \frac{1}{v_m} \left[\frac{x}{100} \cdot Ka \left\{ v_1 - \frac{xv_1 + (100-x)v_2}{100} \right\} + \right. \\ & \quad \left. \frac{100-x}{100} \cdot Kb \cdot \left\{ \frac{xv_1 + (100-x)v_2}{100} - v_2 \right\} \right] \\ & = \frac{1}{2} \cdot \frac{1}{v_m} \left[\frac{x(100-x)}{100} \cdot (Ka + Kb)(v_1 - v_2) \right] \text{ ergs per cc.} \end{aligned}$$

Now, as Desch has recently pointed out (*Trans. Fara. Soc.*, 1915, 251), the atomic volumes of those metals which form uninterrupted series of solid solutions are in all cases very close to each other. (Throughout this paper of Dr. Desch has been of the greatest value to the author and the source of many ideas). The mean atomic volume v_m will therefore undergo very little change from end to end of the series. Thus to a first approximation the increased strain-energy E—

$$E = K \left(x - \frac{x^2}{100} \right) \dots (1).$$

The increased strain-energy due to the solution is therefore a parabolic function of the concentration with a maximum for $x=50$. The experimental curve showing the influence of concentration on the hardness of the alloy and the curve deduced from the strain theory are identical in type.

A quantitative examination of the truth of such an expression for the cause of the increase of hardness also leads to the conclusion that the results are of the right order.

If a material of bulk modulus k is stressed by a force f , less than the elastic limit, the resulting strain-energy induced—

$$= \frac{1}{2} \cdot \frac{f^2}{k}.$$

It is possible therefore to determine what applied stress would produce the same strain-energy as that produced by the solution.

In the present case f may be regarded as an internal pressure comparable with the "intrinsic pressure."

Then, taking as an example the case of the silver-gold alloy with 50 per cent of each metal—

$$\begin{aligned} x &= 50 \quad v_m = 10.2 \quad v_1 - v_2 = 0.031 \\ Ka + Kb &= 27.5 \times 10^{11} \text{ and } k = 12 \times 10^{11}. \end{aligned}$$

$$\therefore f = \sqrt{\frac{27.5 \times 25 \times 0.031 \times 12}{10.2}} \times 10^{11} \text{ dynes per sq. cm.}$$

$$= 6 \times 10^{11} \text{ dynes per sq. cm.}$$

or—

$$6 \times 10^5 \text{ megabars.}$$

It is probable, however, that the hardness of a metal is determined by its intrinsic pressure, and the value of this constant for silver is 1.6×10^5 megabars. The hardness of the 50 per cent alloy of silver and gold is twice that of pure silver, whence the value for f of 6×10^5 megabars may be considered as sufficiently satisfactory.

The high value, however, of the applied stress which would produce the same increase of strain-energy as is produced by the changes of atomic volume may be explained on the assumption that the process of mutual crystallisation of the components of the solid solution does not result in *exact* equalisation of the two atomic volumes, but merely in the tendency towards equivalence. The actual strains would then be smaller than are here calculated, the more so the less exactly did the quality of the atomic volumes ensue. The result then would indicate a considerable divergence of the real conditions from those postulated.

The theory here advanced to account for the characteristic properties of solid solutions has regarded them as being due to the distortion of the crystalline material resulting from the difference of atomic volume of the solvent and solute. Which of these has the larger atomic volume is, from the point of view of the theory, comparatively unimportant. In either case the result is the same—the alloy is hardened. This is directly opposed to the conclusion arrived at by Roberts-Austen in 1888, that the effect of alloying one element with another depends on its atomic volume (*Phil. Trans.*, A, 1888, clxxix., [5], 339). Gold was the element chosen for the experiments, and the generalisation was advanced that the "metals which diminish the tenacity and extensibility of gold have high atomic volumes, while those which increase these properties have either the same atomic volume as gold or a lower one. Further, silver has the same atomic volume as gold, and its presence in small quantities has very little influence one way or the other on the tenacity and extensibility of the metal." There were several elements, however, which occupied abnormal positions in the tables. Aluminium, iridium, and lithium, though possessing high atomic volumes, yet increased the tenacity of the gold, and zirconium, with an atomic volume of 21.8, increased the maximum stress from 7 to 12 tons per square inch.

In 1896, Arnold and Jefferson carried out further experiments on the same lines (*Engineering*, 1896, 176). Their work was supplemented, however, by the examination of the micro-structures of the alloys, which shed considerably more light on the subject. The alloys with 0.2 per cent of lead, bismuth, and tellurium, the elements whose tendencies to produce fragility were the greatest, possessed structures in which each crystal of gold was completely isolated from adjacent ones by cell-walls of the alloying element. These cell-walls completely destroy the cohesion of the whole mass. The crystals of gold, however, were distinctly shown to possess their ductility undiminished. The structures arise from the extrusion, during solidification, of an intergranular eutectic which is the cause of the loss of strength. In such cases little or no connection between the atomic volume and the physical properties can be hoped for. Considering, however, the elements which pass into solid solution as such in the gold, and without the formation of intermetallic compounds, it is found that in all cases the strength of the alloy is increased.

Arnold (*Journ. Iron and Steel Inst.*, 1894, 107), in other work on the same point in iron alloys, showed beyond doubt that the atomic volume has no influence whatever on the physical properties of the resulting alloy, and that, so long as the alloying element passed entirely into solution,

the resulting maximum stress was greater than that of pure iron, whether the atomic volume of the alloying element was equal to that of iron, greater than this, or less.

A few results taken from those published and typical of all the cases where solutions were formed are given in Table I.

TABLE I.

Metal.	At. volume.	Max. stress, tons per sq. in.
Nickel	6.7	26.8
Copper	7.1	34.8
Iron	7.2	21.8
Aluminium ..	10.5	27.0
Phosphorus ..	13.5	29.0

It would thus appear, as Arnold emphatically stated, that the generalisation of Roberts-Austen is not in accordance with the facts either of his own results or those of Arnold. The influence of the alloying element on any metal is, as is demanded by the theory here advanced, to raise the tenacity whether the atomic volume be greater or less.

One other aspect of the effect of the atomic volume in solid solution is of importance. The recent crystallographic work of Barker, Wulff, Gossner, Tutton, (*loc. cit.*), and others has conclusively shown that only such substances as possess similar molecular volumes and distance ratios exhibit the property of forming parallel growths and solid solutions. Desch also has quite recently pointed out the fact that in those series which are completely isomorphous the components have in all cases nearly equal atomic volumes. This point is of the greatest moment metallographically. For example, silver and gold, which possess atomic volumes to 10.23 and 10.20, form solid solutions in all proportions, but silver and lead, with atomic volumes of 10.2 and 18.2, form an eutectiferous series without appreciable miscibility at either end. In the series of iron alloys examined by Arnold, also, carbon with the lowest atomic volume 3.6, and arsenic and sulphur with atomic volumes of 13.2 and 15.7 alone caused the separation of new phases, all the intermediate elements passing entirely into solution. This aspect, again, is in accordance with the theory that in the solid solution there is a progressive replacement of atoms in the space lattice. It is to be expected that where two metals possess similar atomic volumes they will replace each other most readily and thus enter most freely into solid solution. In cases, however, of markedly different volumes the difficulty may well become so great as to virtually prevent solid solution at all.

Passing now to a very brief consideration of the properties of compounds of metals with metals, the same theory still supplies an explanation of their extreme hardness. The interpenetration of the space lattices induces in them a similar change of the atomic volumes, which results in the setting up of elastic stresses which are regarded as the cause of hardness. Since, however, a certain amount of rigidity must be assumed in the space lattice of a compound, so that x atoms of A and y of B always come together in the molecular units of the compound A_xB_y , it is not difficult to understand why these compounds possess not only considerable hardness but are also characterised in almost all cases by intense brittleness.

Many of the ideas which have been extended in the present paper originated with Dr. Beilby. A deformation of the space lattice of a metal as a result of mechanical stress is the first step in the formation of the amorphous modification with which his name is pre-eminently associated. A paper on a similar subject, "The Molecular Structure of Solid Isotropic and Anisotropic Binary Mixtures" has recently been published by Tammann (*Zeit. Anorg. Chim.*, 1914, xc., pp. 297-326). It is concluded that in the space lattice of a binary crystalline solid solu-

tion the two kinds of molecules may be arranged regularly or at random. An irregularity of molecular distribution is probably remedied by annealing more slowly than "zoning" or "coring" due to rapid cooling from fusion. Assuming that the two kinds of molecules are regularly arranged, reasonable agreement is obtained between experimental curves for a cubic crystal—a silver-gold alloy—and those theoretically expected.

Conclusions.

The remarkable hardness and high electrical resistivity of solid solutions of metals point strongly to the fact that they are caused by crystalline distortion similar to that which arises from cold work. This is explained on the theory that the process of crystallisation of such solutions causes an equalisation of the atomic volumes of the constituents. Elastic stresses are thus set up, which, in their turn, increasing the resistance to further stresses, raise the hardness of the mass. Such a theory would lead to a parabolic curve expressing the relationship of the hardness to the concentration throughout the series, with a maximum at composition of 50 atomic per cent of each metal. Such a curve would correspond absolutely with those observed for simple series such as the silver-gold alloys. The same theory would also explain the hardness and fragility of the intermetallic compounds.

A NEW CRYSTALLINE VARIETY OF SILVER.

By TARINI CHARAN CHOUDHRI,
Chemical Laboratory, Government College, Dacca, Bengal (India).

VARIOUS modifications of silver, many of them of somewhat ill-defined character, have from time to time been described. (Carey Lea, *Am. Journ. Sci.*, 1889, xxxvii., 476; xxxviii., 47, 129; *Phil. Mag.*, 1891, xxxi., 238, 320, 497; xxxii., 337; *Am. Journ. Sci.*, 1894, lxviii., 343; Lüdtkke, *Wied. Ann.*, 1894, xcii., 152, 1056; Kohlschütter and Fischmann, *Ann.*, 1912, ccclxxvii., 86). Carey Lea has carried out an extensive series of researches on the properties of silver precipitated from a solution of its salts by ferrous citrate, ferrous tartrate, &c., in the presence of alkalis. His colloidal silver, which is held to be an allotropic modification of the metal, displays almost every shade of colour—blue, red, green, purple, and golden; some of his "precipitates" are very soluble in water and very sensitive to light. According to Lüdtkke (*Wied. Ann.*, 1883, l., 678), however, the mirror and the black silver, obtained by the reduction of silver nitrate with zinc, are allotropic modifications, while the work of Kohlschütter and Fischmann is an attempt to explain the way in which the specular form of native silver, known as hair-silver, is formed.

Experimental.

Spongy silver was first prepared by igniting pure and dry precipitated silver tartrate in a crucible. (The spongy silver examined under the microscope showed no crystalline structure). Nitric acid diluted with an equal volume of water dissolved the silver completely. Strong nitric acid (sp. gr. 1.42), however, from which lower oxides of nitrogen were removed by boiling with carbamide, was allowed to act on the spongy silver at the ordinary temperature. At first some action took place with the formation of silver nitrate, nitrous acid, and oxides of nitrogen, but after a time the solution of silver stopped, and on allowing the mixture to stand with occasional shaking for about a fortnight the remaining silver was converted into long needle-shaped crystals, easily visible to the naked eye.

At first a few thin needle-shaped crystals appeared floating on the surface of the acid liquid which was being shaken; the test-tube being allowed to stand again for some time the crystals gradually increased in quantity, the

larger needles remaining at the bottom of the tube. The nitric acid was decanted off and the crystals were thoroughly washed with distilled water. They had the characteristic white metallic lustre of silver and belonged to the cubic system. The following experiments show that the crystals are nothing but metallic silver:—

(1) A weighed quantity of the crystals was heated on a small cupel in a muffle furnace and the button of silver obtained was weighed—

0.1370 gave 0.1361 Ag : Ag = 99.34 per cent.

(2) A weighed quantity was dissolved in moderately strong nitric acid and the silver precipitated and weighed as silver chloride—

0.2840 gave 0.2826 AgCl : Ag = 99.50 per cent.

This is considered to be a new variety of crystalline silver. Ordinary metallic silver consists of rhombic plates (Hiorns' "Metallography": Silver), which, however, in form and in the mode of formation are quite different. Kohlschütter and Fischmann have described a variety termed hair-silver, but they have only been able to obtain this from silver sulphide or selenide at temperature of about 400°.

Bearing on the Dynamic Theory of Allotropy.

It has been observed, as referred to before, that the tiny needle-shaped crystals which were first formed appeared on the surface of the column of liquid, so that the crystalline silver does not (at the moment of formation) co-exist with the spongy silver at the bottom of the vessel. It has also been observed that the spongy silver at the bottom gradually crumbles into a finer state of division, looking amorphous under the microscope, and this gradually diminishes in quantity, giving rise to crystalline needles at the surface.

As the conversion of spongy silver into crystalline variety takes place at the ordinary temperature in a heterogeneous system, Smits' dynamic theory of allotropy is not applicable to the present case. According to Smits the transformation of one form into an allotrope is not a sudden process, and at the high transformation temperature (*e.g.*, of rhombic sulphur into monoclinic and *vice versa*) each variety is partially miscible in the other at the high transition-temperature, and equilibrium, according to him, being established between different proportions of the different varieties. Benedict also holds somewhat similar views. But such ideas are evidently not applicable to the present case. Tammann's view, however, applies better. According to him allotropic change is due to difference in atomistic arrangements, and it is probable in the present case that the solution-tension of metallic silver at the particular condition being small, the particles of silver, which are first produced from spongy silver, are drawn up by the capillary force of the liquid column to its surface, where they orient themselves regularly in a different space-lattice, giving rise to the beautiful needles.

Summary.

Spongy silver, prepared by igniting pure silver tartrate, was treated at the ordinary temperature with strong nitric acid (*sp. gr.* 1.42) from which lower oxides of nitrogen had been removed by boiling with carbamide. At first some action took place with the formation of silver nitrate and nitrous acid, but after a time the solution of silver stopped, and on allowing the mixture to stand with occasional shaking for about two weeks the remaining silver was converted into long needle-shaped crystals easily visible to the naked eye; slender needles, which are first formed, appear floating on the surface of the acid liquid. This is considered to be a new variety of crystalline silver, belonging to the cubical system.

The author desires to express his indebtedness to his professor, Dr. E. R. Watson, who took an active interest in course of this work.—*Journal of the American Chemical Society*, xxxvii., No. 9.

THE EXTRACTION AND SEPARATION OF THE RADIO-ACTIVE CONSTITUENTS OF CARNOTITE.*

By H. M. PLUM.

(Concluded from p. 233).

Polonium and Radio-lead.

THE filtrates from the first three treatments of the ore, *i.e.*, with carbonate of soda, with hydrochloric acid, and with nitric acid, were examined for polonium and radio-lead, which were found only in the chloride solution. When the filtrate from the carbonate extraction was examined for polonium by adding to it a little bismuth nitrate and then precipitating with hydrogen sulphide, no polonium was found in the bismuth sulphide. The sulphides, obtained by treating the hydrochloric acid filtrate in a similar manner, were comparatively active. These sulphides were dissolved in boiling concentrated nitric acid, sulphuric acid was added to the solution, and the lead was separated from the bismuth by the usual analytical methods. It was not necessary in any of these experiments to add any lead salt to carry down the radio-lead, since the original ore contained small quantities of that element. The lead sulphate which was only slightly active at first, greatly increased in radio-activity in the course of ten months. The bismuth and polonium, after being separated from the lead, was further purified by precipitating them with ammonium hydroxide. This precipitate was then filtered out, and, after being dissolved in a few drops of hydrochloric acid, the solution was examined quantitatively for polonium by depositing it on copper. In the last kilogram lot the bismuth chloride obtained, as described above, was diluted with water up to 250 cc., enough hydrochloric acid being added to keep the bismuth in solution. Five cc. samples of this solution were further diluted with about the same volume of water, and introduced into a beaker containing a clean piece of copper foil, the under side of which had been covered with wax. Under these conditions the polonium deposited on the copper, the process being hastened by stirring with a current of air, so that in thirty or forty minutes a large part of the polonium had collected on the copper foil. In an experiment which had run thirty minutes, the first foil was removed, and a second and a third were introduced into the same solution for about the same length of time. The activity of the polonium deposited on these three foils varied as 11 : 2 : 1/6, showing that more than 80 per cent of the polonium, in the 5 cc. sample, had deposited on the first copper foil in thirty minutes. When the total polonium activity was calculated it was found that about 50 per cent of the amount in the original ore had been recovered in the filtrate from the hydrochloric acid extraction. When the nitric acid solution was treated in the same way as the hydrochloric acid filtrate the bismuth sulphide obtained did not contain any polonium.

Ionium.

In this research great effort was made to discover what course the ionium took and how it could be recovered to best advantage. The filtrate from each of the first three extractions, *i.e.*, with soda, with hydrochloric acid, and with nitric acid—was therefore carefully examined. As this ore contained only small quantities of the rare earths a little thorium or cerium salt had to be introduced into the filtrate in order to get a precipitate on the addition of oxalic acid. The oxalates thus obtained should have carried down whatever ionium there was in the filtrate. When the solution from the sodium carbonate extraction was examined in this way no ionium was found. Likewise the filtrates from the hydrochloric and nitric acid extractions showed but very little more activity than could be accounted for by the thorium added. From these

* *Journal of the American Chemical Society*, xxxvii., No. 8.

results it was evident that the ionium had either escaped detection or had not yet been removed from the insoluble siliceous residue. An examination of the latter, by means of the emanation method, showed that approximately 95 per cent of the radium had already been removed from the original ore. But the α -ray activity of the residue, as measured by thin films, was considerably greater than could be accredited to the 5 per cent of radium left therein. In order to remove this radio-active substance the residue was finally treated with sulphuric acid, as already described, because it was believed that if any radio-active matter were dissolved by this acid it would not be radium, but might be ionium. Further, it was thought that the rare earths might be present in some form like the fluorides, and that drastic treatment, such as boiling with concentrated sulphuric acid, would be required to remove them. This method proved successful, for, when this mass was digested with boiling water, the filtrate not only contained all the vanadium left in the residue, but also the greater part of the ionium. When a small amount of thorium nitrate was added to the filtrate thus obtained and the thorium precipitated as oxalate, it always possessed much greater activity than had been observed in the filtrates from any of the other extractions. The ore did not contain enough, if any, thorium to carry down the ionium without the addition of thorium. But as thorium and ionium cannot be separated by any known reaction and as we wished finally to obtain ionium mixed with a minimum of thorium, cerium was added to the sulphate solution instead. It was found difficult, however, to precipitate cerium oxalate in acid solution in the presence of vanadium and iron, but it could be accomplished by almost neutralising the sulphuric acid with ammonium hydroxide, and then adding oxalic acid until it had nearly saturated the solution. To get the ionium in a more concentrated condition the resulting cerium oxalate was thoroughly shaken with a solution made by dissolving 40 grms. of dry sodium carbonate and 20 grms. of sodium bicarbonate in 400 cc. of water, 10 cc. of which were used for each grm. of cerium oxalate. Under these conditions a large portion of the ionium was dissolved while the cerium remained behind as an insoluble carbonate. When the cerium carbonate thus obtained was dissolved in nitric acid, the solution neutralised with ammonia, and then hydrogen peroxide added, upon heating to 70° the balance of the thorium and ionium were precipitated. The residue carrying the ionium was very small; it probably consisted essentially of thorium, which may have been contained originally as an impurity in the cerium used. A test made on some of this material by means of the emanation method showed not the slightest trace of radium, and films made from these ionium residues remained constant in activity for ten months. When the ionium was separated from the last kilogram of ore in the manner just described and its activity measured by the method given in a preceding paragraph, the results showed the recovery for this element to be about 61 per cent of the total amount calculated for the original ore.

Actinium.

Just as in the case of the other radio-active elements the filtrates obtained from treating the ore in succession with carbonate of soda, with hydrochloric acid, and with nitric acid, were examined for actinium. As actinium is said to occur with ionium in the rare earth precipitates, all the precipitates of cerium and thorium oxalates made in studying ionium were likewise examined for actinium, but there was no evidence to show that the actinium accompanied the ionium in the course the latter took before being recovered from this ore. Actinium, however, was found to be carried down with the barium sulphate containing the radium. That it might be the more completely recovered small amounts of barium chloride were added, and several precipitations of the barium sulphate made in the filtrates from the hydrochloric and nitric acid extractions. These combined sulphates were then fused with a

mixture of sodium and potassium carbonate in molecular proportions, the barium carbonate was thoroughly washed, and then converted into chloride. On adding ammonium hydroxide to this solution a precipitate formed which, although but slightly active at first, grew in activity until the increase amounted to fifteen- or twenty-fold, the rate of increase being about that expected for actinium initially free from radio-actinium and actinium X. The actinium, moreover, was not all removed from the barium in this way, for, by adding 1 or 2 grms. of an aluminium salt to the radium barium solution and then precipitating the aluminium with ammonium hydroxide, a precipitate was obtained which also increased many-fold in activity. To prevent any radium from being held by the aluminium hydroxide the latter was dissolved and reprecipitated three times, and the activity of the actinium under these conditions was then measured. In the experiments on the last kilogram of ore 2 grms. of aluminium nitrate were added to the barium solution and precipitated in the manner described above. The aluminium hydroxide thus obtained increased in activity about thirty-five-fold in twenty-five days. A second precipitation using the same amount of aluminium nitrate gave a precipitate which, while not so active at first as the former one, increased more than seventy-five-fold in the same interval of time. From these results it is clear that the actinium contained in the barium radium solution cannot be separated completely by a single precipitation of aluminium hydroxide in this solution. The percentage of actinium found by the above treatment was 52 per cent of the total amount as calculated in a preceding paragraph.

Summary.

In this paper a careful study has been made of a Colorado carnotite, and a satisfactory method worked out for the extraction of the radio-active ingredients. Several of the commercial methods now in use for removing vanadium and uranium from a carnotite ore have been examined and modified so as to be effective in treating our ore which was found not to be a pure carnotite, but a mixture of this mineral with a vanadiferous silicate containing the vanadium in a condition difficult to remove. The method finally adopted gives good results. The uranium is removed by boiling the carnotite concentrates with a sodium carbonate solution, precipitated as uranyl sodium carbonate by merely concentrating the filtrate, and the soda is again recovered. The radium, actinium, and radio-lead are contained in the filtrate obtained by boiling the residue insoluble in soda solution with hydrochloric acid. That part of the radium still held in the residue is then removed with boiling nitric acid. The ionium is finally recovered from the residue by boiling with sulphuric acid, and is then concentrated with cerium rather than with thorium, from which it cannot be separated by any known reaction. A summary of the processes used and the results obtained from the last kilogram of carnotite concentrates is here given.

One kilogram of carnotite concentrates was boiled for several hours with 2 litres of a solution containing 400 grms. of anhydrous sodium carbonate. The filtrate yielded 88.1 grms. of uranyl sodium carbonate, $\text{UO}_2\text{CO}_3 \cdot 2\text{Na}_2\text{CO}_3$, which represented 88 per cent of the total uranyl in the sample. The filtrate still held 2 per cent of the uranium in solution. A second treatment of the ore with 300 grms. of sodium carbonate, under the same conditions as above, dissolved out only 2.8 per cent of the uranium. The residue was treated with 400 cc. hydrochloric acid diluted with about a litre of water, and boiled about eight hours. The barium radium sulphate separated from the filtrate weighed 7.36 grms. The residue was next heated a day with 200 cc. of nitric acid diluted with about a litre of water. The barium radium sulphate precipitated in this filtrate weighed 0.453 grm. The percentage of radium in these combined sulphates was 89.8 per cent of the total amount in the ore. Reprecipitations of barium sulphate in the two acid filtrates carried down 2.7 per cent more of

the radium. The lead sulphate, separated from bismuth and containing the radio-lead, weighed 0.49 grm. The polonium precipitated with bismuth and then deposited on copper was 50.1 per cent of the total amount in the ore as calculated from the ranges of the radio-active elements. The residue was finally treated with twice its weight of sulphuric acid after being diluted with about an equal weight of water, and then heated until most of the sulphuric acid had escaped in fumes. The activity of the ionium found in this solution was 61 per cent of the total amount in the original carnotite, as calculated in a preceding paragraph. The residue left after all extraction processes weighed 507 grms., 50.7 per cent of the original ore used. Its activity as measured by the emanation method showed that only 4.2 per cent of the radium still remained in the residue.

NOTES ON RARE MINERALS IN MADAGASCAR.

By T. P. WAITES.

1. Uranium, Niobium, and Tantalum Minerals.

The centre of Madagascar, in the districts of Antsirabe and Betafo, about one hundred miles south-west of Tananarive, is extraordinarily rich in uranium and niobium minerals, which occur in pegmatite.

Very little, however, was known of the occurrences till the end of 1911, when the district was visited by M. Lacroix, of the Académie des Sciences de Paris.

On one claim (2500 hectares) is found blomstrandite, betafite, samiresite, ampingabeite, brown garnet, monazite, euxenite, amazonite, columbite, tantalite, bismuth, uranite, copper, beryl, amethyst, orangeite, sphene, and oxide of manganese. Betafite, samiresite, and ampingabeite (related to pyrochlore, variety hatchettolite) are minerals which prior to 1912 were unknown to science, and their average uranium oxide content is approximately 22 per cent (see analyses attached). It is only during the past few months—say only during this year—that any market has been found for these uranium ores. The method of treatment for pitchblende and for the extraction of its radium content was known, but it was not certain that the same methods would apply in the case of these new minerals. Recently it has been found possible to treat them, and I venture to predict that the district will become the premier producer of uranium and enable radium to be obtained at a price which will render it much more freely available for medical purposes than it has been hitherto.

Betafite, samiresite, ampingabeite differ from each other in their chemical constituents, as also they differ from blomstrandite (see analyses attached). They are named from the places at or near which they were first found—viz., Betafo, Samiresy, Ampangabe.

The districts around Betafo and Antsirabe are decidedly volcanic. There is no active volcano here nor in any other part of Madagascar, and authorities differ much in the hypothetical estimation of the geological age of the volcanic activity, but there are craters made up of scoria or volcanic ash, horse-shoe shaped, lop-sided and broken, on the south-east, whence comes the trade wind, prevailing for nine months out of the twelve. Others are of lava and have flooded the country in parts for miles around. Here and there are patches of columnar basalt. There are also many volcanic necks, rounded, fez-shaped, or conical, and east, west, north, and south are hot springs and cool "mineral water" springs side by side, whose waters also contain uranium salts, and have from time immemorial been resorted to by "natives" on account of their medicinal qualities without the natives knowing the why or wherefore.

The Vavavato range consists of hornblende gneiss. This range has the appearance of having been tilted up by volcanic action all along its eastern side. Gneiss is certainly the prevailing rock in the archæan region—i.e., two-thirds of the island.

To turn to the pegmatites, I find that they are composed of orthoclase felspar (a mineral which gives the whole range of Vavavato a pinkish colour), quartz, hornblende (the hornblende is sometimes very much decomposed and of a waxy nature in places, white or streaked with red), and what is locally and generally termed biotite, or black mica, but is really uranite. The black-brown garnety mineral, which carries only 4 per cent of uranium oxide, is a negligible quantity commercially, not being rich enough in uranium. Sometimes, on breaking up large pieces of this, beautiful betafite crystals are found within.

I have tried to touch lightly on the salient points of this interesting district—its niobotantalotitanates, its pegmatites, its geological formation. All the constituents of the pegmatite are radio-active and uraniferous. Even the felspar carries 1 per cent uranium oxide. Further prospecting has shown that uranium ores occur over a very considerable portion of the archæan region and not in the pegmatite only. Uranium is found from Cape St. Marie, the southern point of the island, to as far north as Ankazobe, about fifty miles north-west of Tananarive, and from the Indian Ocean to the Bongolava range. The niobates are found not only in the form of crystals but also as veins in the pegmatite and as veins in the schists and gneisses, the outcrops being traceable for many kilometres. One of them persists for 70 kilometres, and one sample taken from it assayed 2.87 per cent U_3O_8 . Parallel with it is another vein carrying thorium, two assays showing 7.8 and 2.78 per cent ThO_2 . The analysis of these minerals is difficult, but my experience has been that the uranium content of ores as shown by assay and by the electroscope in expert hands is nearly identical.

The following are analyses of four different uraniferous crystals:—

	Bloms- trandite.	Betafite	Sami- resite.	Ampan- gabeite.
Nb_2O_5	23.30	34.80	45.80	34.80
Ta_2O_5	28.50	trace	3.70	8.90
TiO_2	10.87	18.30	6.70	4.90
SnO_2	0.30	0.30	0.10	—
ThO_2	—	1.30	—	2.50
UO_3	18.10	26.60	21.20	19.40
Bi_2O_3	0.40	—	—	—
Al_2O_3	—	2.10	0.74	2.10
Fe_2O_3	—	2.87	—	8.60
FeO	1.35	—	1.06	—
$(Ce, La, Di)_2O_3$	2.50	0.60	0.20	0.60
$(Y, Er)_2O_3$	0.30	0.90	—	4.00
MnO	0.50	—	—	—
MgO	0.20	0.40	—	—
CaO	4.00	3.45	—	1.50
PbO	—	—	7.35	—
K_2O	—	—	0.30	—
Loss on ignition	9.60	7.60	12.45	12.40
	99.92	99.22	99.60	99.70

These analyses are from Paris. Prof. Lacroix "On the Uraniferous Niobotantalotitanates (radio-active) of the Pegmatites of Madagascar." Séance de l'Académie des Sciences, April 22, 1912.

II. The Uranium Phosphate of Vinaninkarenena, near Antsirabe.

The phosphate of uranium is exposed by a deep cutting made by a river flowing south through the lacustrine deposits, about ten kilometres south of Antsirabe. The uranium salts thus exposed have evidently been precipitated on a thin layer of (tourbe) peat, decomposed vegetation of some sort, favourable to the deposition and crystallisation of these salts, which salts are not found throughout the "clay" but in one thin layer only on the decomposed vegetation. The whole of this lacustrine deposit on the old lake bed at Antsirabe contains this uranium phosphate. As this deposit is about ten miles distant from the mineral springs of to-day, I think it is

probably not deposited from the mineral springs, but is a product the result of oxidation, disintegration, and the action of water on the uranium ores in the surrounding hills.

In the Infanja marsh, north of Itasy, are mineral springs, hot and cold; north of this marsh, in an area where uranium oxide is found, is a cold spring of mineral water, carrying uranium salts in solution. This spring gushes through the gneiss, not with a constant flow like the mineral springs at Antsirabe, but pulsating, and deposits its uranium in a manner I have not found elsewhere in the island. I put my hand as far as I could into the spring, and found the "pipe" of the spring filled with small rounded stones, in appearance, shape, and colour like hard peas. These "pea stones" are evidently accretions of uranium from solution around small specks of sand or other foreign matter, which have been blown into the spring, in rings of brown, lemon, and black colour, the shape being due to the beating or pulsating action of the spring and the friction of stone against stone, giving all of them a spherical shape, the colour, inside and out, being identical with the uraniferous ores found elsewhere.

I do not give this example as proof that the carnotite of Utah and the autunite of Antsirabe are *not* deposits from uranium salts in solution in the waters of mineral springs, but it is proof that uranium in solution does not necessarily crystallise as the bright green or canary yellow of the carnotite and autunite. Where the uranium phosphate is found there are no mineral springs nearer than ten kilometres; there may have been in some past geological age, but there is no evidence in the shape of calcareous sinter deposits, such as one sees at Antsirabe, and from which Antsirabe takes its name. These "pea stones" (they are not the aragonite of the Carlsbad springs) are radio-active and uraniferous.

The district around Infanja marsh is volcanic, probably of comparatively recent date, in any case more recent than the volcanic activity which produced the patches of columnar basalt near Betafo.

Uranium phosphate is found also in the district of Analava, in the north-west of the island, near to the sea.—*Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, xvi., No. 8.

centage of water than the hydrated silica or opal of which ordinary siliceous spicules are composed. The colloscleres lie in vesicles in the mesoglaea, but these vesicles do not represent the mother-cells or scleroblasts by which they are secreted.

On the contrary, the collosclere is an extra-cellular product, and first appears as a knob on the outer surface of the cell-membrane of a large spherical scleroblast. The colloscleres may be homologous with isochelæ, but the supposed intra-cellular origin of the chelate and other microsccleres must be reinvestigated before this point can be established.

"Classification of the Reptilia." By E. S. GOODRICH, F.R.S.

"Experimental Production of Congenital Goitre." By R. McCARRISON, M.D.

The following selected candidates were elected as Fellows:—Edwin Henry Barton, William Robert Bousfield, Sidney George Brown, Ernest George Coker, George Gerald Henderson, John Edensor Littlewood, Alexander McKenzie, John Alexander MacWilliam, Joseph Henry Maiden, Henry Harold Welch Pearson, James Arthur Pollock, Sir Leonard Rogers, Cresswell Shearer, D'Arcy Wentworth Thompson, and Henry Woods.

CHEMICAL SOCIETY.

PRESIDENTIAL ADDRESS, BY DR. ALEXANDER SCOTT, F.R.S.*

(Continued from p. 249).

THE celebration of the jubilee of the discovery of mauve and of the coal-tar colour industry fell most opportunely during the Presidency of the late Prof. Meldola, to whose untiring energy and profound knowledge of the subject and everything connected with it the great success of the celebration was largely due. In acknowledging the address presented by the Chemical Society Sir William Perkin mentioned that for seventeen years he had been a Secretary of the Society and for two years its President. When mauve was discovered in 1856 the membership was 261, and in 1906 it was 2700. To the subscribers to the Perkin Fund we owe the marble bust which adorns our Library, as well as an addition of £2704 3s. 8d. to our Research Fund, which a few months before had received a second donation of £1000 from the Worshipful Company of Goldsmiths. These have raised the annual income of the fund almost to £350, which is still far from sufficient to meet the many applications worthy of support in the way the Research Fund Committee and the Council would desire. I am glad that the addition of £2500 to the fund which I have been privileged to announce to-day will assist the Council in making somewhat larger grants to those who so richly deserve every encouragement which our Society can give.

In these somewhat scrappy notes in which I have dealt with the earlier part of our history more fully than in the later one association deserves mention, though its activities are now paralysed. I refer to the formation of the International Association of Chemical Societies, which met for the first time in Paris in 1911, then in Berlin in 1912, and although it was arranged that it should meet in London in 1913 various circumstances arose which led to the meeting being held in Brussels. Amongst the reasons for the change of meeting-place was the unconditional gift of 250,000 francs by M. Ernest Solvay as well as of an annual income of 37,500 francs and of a handsome set of rooms in the Solvay Institute there for the permanent offices of the Association. For obvious reasons no meetings were held in 1914 and 1915. I fear that the offices

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

May 11, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Seventh Memoir on the Partition of Numbers. A Detailed Study of the Enumeration of the Partitions of Multipartite Numbers." By Major P. A. MACMAHON, F.R.S.

"On Legendre's Function $P_n(\theta)$ when n is Great and θ has Any Value." By Lord RAYLEIGH, O.M., F.R.S.

"Occurrence of Gelatinous Spicules and their Mode of Origin in a New Genus of Siliceous Sponges." By Prof. A. DENDY, F.R.S.

Collosclerophora arenacea, n. gen., n. sp., a sand-sponge from Australia, contains an entirely new type of spicule, for which the name *collosclere* is proposed, and similar spicules are met with in another species from the Indian Ocean. The collosclere differs from all spicules previously known in the fact that it consists of a gelatinous material, contracting on the addition of alcohol and swelling up again on the addition of water.

Evidence is brought forward to show that these spicules are composed of colloidal silica containing a higher per-

* Delivered at the Ordinary Scientific Meeting, April 6, 1916.

and all the documents and endowments are at present in the hands of the Huns. Any meetings in the immediate future are not likely to be of the same international and harmonious character as those of the past have been.

As I have already indicated, the importance of stimulating and encouraging research was recognised from the first by the founders of our Society, and president after president has insisted not only on its absolute necessity if we are merely to hold our own in commerce and manufacture, but that it must be strenuously cultivated by securing for this purpose the highest talent and the best brain-power if we are to make any progress. The making of discoveries and the wrestling from nature of her secrets is the paramount duty of every scientific man. This is agreed to tacitly by all, but tacitly it still remains. This negative or neutral attitude is maintained partly because the public in general, and in a more especial degree the so-called well-educated classes who have been to public schools and the older universities, have no conception of what research means. The classical scholar pure and simple adds but little to the sum of human knowledge. He turns over and over again that which has been accumulated in past ages, extracting what was buried by those who went before and who did make some real progress worth recording. He always puts me in mind of a ploughman, say on the field of Waterloo, who may find a leaden bullet really fired from a musket a hundred years ago (and not planted since). He wonders which side fired it, whether it hit anyone, and many other such problems arise in his mind, all of which may be perfectly legitimate objects of inquiry and require much ingenuity for their complete solution. They may even be of considerable interest to the anxious inquirer, but of what use can they be to anyone? The classic may retort, "Of what use are many of your chemical researches to anyone?" The reply is that "knowledge is power." Every addition to our knowledge, be it of a new element, a new compound, a new reaction, or a new law of nature—all such knowledge increases the power to make still further advances and confers a greater power to overcome difficulties, and in the end to increase human happiness and the advancement of civilisation.

Let us take some simple examples of what research has done in the past such as everyone can appreciate, and realise the connection between the quest of knowledge for its own sake and the results of the application, it may be many years afterwards, of the knowledge so discovered to the manufactures and requirements of the present day.

For this purpose we may divide research into two distinct categories, each of which requires for its successful prosecution a different type of mind and training.

The devotee of the first type seeks the mere addition of fresh knowledge to that already recorded, fresh ways of overcoming natural difficulties, new ways of utilising energy and of directing it. The second type starts on the definite quest for the solution of a determinate problem, it may be the building up of some compound occurring in nature, the profitable extraction of a metal from its ores, or the preparation of a substance which shall have definite properties.

Many examples of these are known to all present, but perhaps, as "The Sceptical Chymist" would remark, "it may well be for divers reasons that some of them be recorded here."

Researches of the first type may well be exemplified by the experiments of Cavendish in 1785 on the composition of the atmosphere when he converted the nitrogen and oxygen into nitric acid, proving that it was formed but required more oxygen to be added, and at the same time recording that a small residue of some gas remained uncombined, "so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid we may safely conclude that it is not more than 1/120th part of the whole." This discovery lay dormant for more than a hundred years until Lord Rayleigh proved that pure nitrogen prepared

from a compound was lighter than the so-called nitrogen from the atmosphere, which led in his and Sir William Ramsay's hands to the detection and isolation of argon, the first element of a type hitherto unknown in that it seems to have physical without chemical properties, and other members of the same group were shortly afterwards discovered and separated from the atmosphere and other sources. Lord Rayleigh's method of preparing argon from the air was but a modification of Cavendish's original experiment, but it led incidentally to his making a determination of the amount of energy required to prepare nitric acid from air and oxygen. In his Presidential Address to the British Association at Bristol in 1898 Sir William Crookes, with his usual perspicacity and directness, pointed out what *must* happen if the population of the world went on increasing at the rate it was then doing, and that the only means of averting certain catastrophe was to obtain the nitrogen of the air in a form suitable for plant life before the supplies of natural nitrates should be completely used up. The experiments of Cavendish and of Rayleigh now gave a theoretical clue to one solution at least of the problem. A great industry has grown up, although *not in this country, where these discoveries were made*, but in Norway, Switzerland, and America, in which atmospheric nitrogen is converted into calcium nitrate and nitrite.

Similarly, Moissan's investigations into reactions which take place at temperatures producible by means of the electric furnace led to the discovery of many new compounds, of which the carbides, compounds of the metals with carbon, were soon shown to be of high technical importance. One of them, the well-known calcium carbide, was found to yield practically pure acetylene on treatment with water, and for this purpose it is manufactured in quantity. Other reactions, such as the formation of cyanides in blast furnaces, previously observed by Dawes in 1835, were proved by Bunsen and Playfair to be dependent on the atmospheric nitrogen, and led to experiments being made with calcium carbide and nitrogen. The reaction, although not giving a cyanide, gave calcium cyanamide, from which either ammonia or cyanides can readily be obtained. In these industries the original experiments on which they are based were made solely with the object of increasing our knowledge both in extent and in accuracy, but without much further research of an accurate and often apparently useless nature these could never have been brought to a successful conclusion on a practical scale. The effects of temperature and pressure on the rate and the extent of combination of the oxygen and nitrogen had to be determined, and also in the carbide process the effect of adding various salts to the mixture of lime and carbon, as well as to the carbide produced, to find out whether these might increase the rate of combination of the nitrogen either by some surface action or by rendering the mass more porous, or by permitting the action to go forward at a lower temperature.

Important and interesting from the philosophical aspect, in view of the theories as to the constitution of salts then being discussed, as were the experiments on the decomposition of water by Nicholson and Carlisle and of the alkalis by Davy, the part which these researches were to play in their application to the arts at no distant date was but dimly realised. Davy in 1826 remarks "that the true origin of all that has been done in this department of philosophy was the accidental discovery by Nicholson and Carlisle of the decomposition of water by the pile of Volta on April 30, 1800, which was immediately followed by that of the decomposition of certain metallic solutions and by the observation of the separation of alkali on the negative plates of the apparatus."

Sodium is now manufactured by tons by Davy's process of electrolysis sodium hydroxide, as is calcium from calcium chloride. The electroplating and electrotyping industries depend on the same electrolytic decomposition of metallic salts for their success. Hydrogen, oxygen, and chlorine are all similarly prepared. From Faraday's

experiments, made in the same laboratory on liquid chlorine and other liquid gases, another industry has grown up, whilst his discovery and separation of benzene from oil-gas has originated one of the most interesting and the most complex of all the chemical industries, which has its origin in the manufacture of coal-gas and the separation from that and its by-products of a whole host of similar compounds and their transformation into dyestuffs, perfumes, drugs, and explosives. Even now there seems to be no limit to the possibilities still latent in coal-tar, that smelly mine of untold wealth both as hard cash and in chemical theory.

Of victories due to the second type of research no better examples could be given than the investigations which led up to the preparation on a manufacturing scale of alizarin, the colouring matter of madder root, and of indigo, which is derived from many leguminous plants grown for its sake in India, China, and elsewhere. Alizarin was proved to be closely related to anthracene, a solid which existed amongst the by-products of coal-gas, and along with naphthalene was at one time considered a nuisance as tending to choke the gas mains by being deposited in them. The naphthalene, for a long time of but little value, is now utilised in making indigo and other dyestuffs. Indigo was known to be closely related to aniline in 1826, and other syntheses besides that from naphthalene are based on a knowledge of this. By the manufacture of these dyes from coal-tar products millions of acres of land are set free for the growth of other crops. Before accomplishing the feat of manufacturing indigo at a price which could compete with indigo from the plant the Badische Anilin and Soda-Fabrik had to expend a million sterling on experiments and apparatus for the purpose.

As an example of research prosecuted to attain a definite end, not to prepare a compound already known, but by knowing the properties of compounds and the changes produced in these by changes in constitution, none is better fitted to illustrate the persistent and strenuous nature of the work of the highly trained chemist than that involved in the discovery of salvarsan.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, May 12, 1916.

Prof. C. V. BOYS, F.R.S., President, in the Chair.

A PAPER, entitled "*The Latent Heats of Fusion of Metals and the Quantum-theory*," was read by Dr. S. H. ALLEN.

The latent heat of fusion is identified with the energy necessary to counterbalance that of a certain number of "oscillators" concerned in holding together the crystalline structure. Assuming that the energy of an oscillator having a vibration frequency ν is—

$$RT \times \frac{x}{e^x - 1},$$

where x stands for $h\nu/RT$, it is found that the atomic heat of fusion of a metal can be calculated with fair accuracy by the formula,—

$$AL = cNRT \times \frac{x}{e^x - 1},$$

Here A denotes the atomic weight, L the latent heat, and c the ratio of the number of oscillators in question to the number of atoms. Thus, the number of oscillators in 1 gm. molecule is Nc , where N is Avogadro's constant. It is found that to the factor c must be assigned a value which is either unity or a simple fraction. The frequency at the temperature of the melting-point is calculated by means of the formula of Lindemann. The application of Debye's theory is also discussed.

DISCUSSION.

Dr. R. S. WILLOWS agreed with Dr. Allen that the quantum-theory was still in a very speculative state. He referred to the statement in §1, that "*The energy supplied to melt the solid may be identified with the work that must be done to break the bonds which impart to the solid its crystalline structure.*" This seemed to rule out of consideration the case of amorphous solids. It is supposed that some of the alterations produced in a metal by treatment such as rolling are due to some of the molecules becoming amorphous. Could the theory be extended to deal with the change from the crystalline to amorphous states?

Dr. ALLEN thought the change from crystalline to amorphous conditions was the same as from crystal to liquid.

Prof. BOYS—Would not that imply that there was no latent heat in amorphous material?

Dr. ALLEN agreed that that would be implied.

A paper, entitled "*Lenses for Light Distribution*," was read by Mr. T. SMITH.

The principle on which lenses for securing a required distribution of light from a given source have been designed is illustrated by a two-dimensional example. The principle employed is to divide the incident and emergent energy into a number of equal parts, and compute the lens system so that the rays which separate off these portions of incident light from one another are refracted as rays which separate the corresponding portions of the emergent light. The surfaces obtained are, in general, of varying curvature, and the lenses must therefore be moulded. It is shown how the effect of the finite size of the light source may be determined.

DISCUSSION.

Mr. R. S. WHIPPLE asked how the results obtained with lamps designed on the lines discussed in the paper compared with those previously employed, which had been evolved, he presumed, simply by the survival of the fittest? Were lenses of this type used at first cast or were the surfaces finally worked?

Mr. SMITH stated, in reply, that the lamps previously in use gave very unsatisfactory results. Their performances varied greatly among themselves, and there did not appear to be any principle underlying their design. In many cases the lenses were not even symmetrically made, and the number of dioptric elements employed depended entirely on the whim of the maker. Some of these lenses had been ground, but he was not aware that they had been used except by the Admiralty. The new lenses, on the other hand, were giving very satisfactory results, despite the fact that some manufacturers had not yet quite realised the ideal conditions. The lenses were moulded and then, in some cases, glazed by what he believed was a secret process.

A paper, entitled "*The Choice of Glass for Cemented Objectives*," was read by Mr. T. SMITH.

The strict fulfilment of the mathematical conditions for freedom from colour, spherical aberration, and coma, for objects at varying distances from a thin cemented doublet lens, necessarily demands a change in the kinds of glass as the position of the object is changed. The paper describes a method by which the proper glasses can be determined by using a glass chart on translucent paper, in conjunction with diagrams calculated for the purpose, as a slide-rule. With most glasses the solution to the problem is imaginary, and formulæ are given for calculating the boundary separating real and imaginary solutions by solving a quadratic equation. In practice it is found that the curves for all real images lie very close to one another. Notwithstanding this, a numerical example shows that there will be a perceptible difference in the definition obtained if in place of the theoretically necessary type a kind of glass is substituted which does not differ greatly from the other, and lies on a curve giving perfect correction for another real magnification. It is

further shown that when no real solution is forthcoming for a double lens a real solution will in practice be obtained by adopting a triple objective made of the same glasses.

NOTICES OF BOOKS.

A Handbook of Colloid Chemistry. By Dr. WOLFGANG OSTWALD. First English Edition, translated from the Third German Edition by Dr. MARTIN H. FISCHER with the assistance of RALPH E. OESPER, Ph.D., and LOUIS BERMAN, M.A. London: J. and A. Churchill. Pp. xii. + 278. Price 12s. 6d. net.

This treatise on colloidal chemistry is so well known by all workers in this branch that it is probably quite as unnecessary to call attention to it as it is to enlarge upon the immense practical importance of the subject. It is rather surprising that although seven years have elapsed since the German original edition first appeared, it has not previously been rendered into English, this translation having been prepared from the third German edition. The translators have performed their task with great care, and have undoubtedly done good service to science in making the book known to a wider public. The theory of the colloidal state, the relations between the physical state and the general properties of colloid systems, the energetics of the dispersoids, &c., are treated at length in the first part of the book, while Part II. on special colloid chemistry deals with the mechanical properties of colloid systems, and the classical work of Perrin, Smoluchowski, and others is excellently explained.

Composition of the Natural Gas used in Twenty-five Cities. By G. A. BURRELL and G. G. OBERFELL. Washington: Government Printing Office. 1915.

IN this bulletin an account is given of the investigation undertaken by the authors of the properties and composition of the natural gas which is used in twenty-five cities in the United States. Among the results which are arrived at attention may be called to the fact that methane was found to be present in five cases only, although it has generally been assumed to be the predominant constituent. The explosibility of mixtures of natural gas and air was determined, and it was shown that hydrogen, carbon monoxide, oxygen, and olefine hydrocarbons are always absent. Helium was sometimes found, from a trace to 1.84 per cent. The physiological effects of natural gas were also investigated, and it was found that a large proportion is necessary to produce suffocation.

OBITUARY.

LADY CROOKES.

UNIVERSAL sympathy will be felt with Sir William Crookes, who has suffered the heaviest of all bereavements by the death of his wife on May 10. Lady Crookes, whose maiden name was Ellen Humphrey, was born on January 31, 1836, and was therefore in her eighty-first year. She was married to Sir William on April 10, 1856, and from the earliest times took the liveliest interest in his scientific work, helping him, amongst other things, in delicate chemical weighings and the working out of the calculations connected therewith. Her devotion to and interest in his work formed a great incentive, and in no small degree contributed to his successful efforts in research. Theirs was the first private house in England in which electric light was introduced, and Lady Crookes

helped her husband greatly in carrying out the installation and designing the ornamental work. She was a familiar and ever-welcome figure at scientific gatherings, to which she frequently accompanied her husband, and was able to be present with him at the reception given after his election as President of the Royal Society in the year 1913. Sir William and Lady Crookes celebrated their golden wedding in 1906, when they were able to welcome a large number of their friends and acquaintances, and were also the recipients of letters and telegrams of congratulation from all parts of the world. Lady Crookes was spared to celebrate quietly with her husband last month the almost unique event of a diamond wedding, but she was then in failing health, and passed away peacefully on May 10. Several sons and a daughter survive her.—*Nature*, May 18, 1916.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 13, March 27, 1916.

This number contains no chemical matter.

No. 14. April 3, 1916.

Isomeric Acetyl Derivatives of Nataloin and Homonataloin.—E. Léger.—When acetic anhydride acts on nataloin in presence of $C_2H_3NaO_2$ three isomeric acetyl derivatives, β , γ , and δ respectively, are obtained. If zinc chloride is substituted for $C_2H_3NaO_3$ the same products are obtained, the only difference being that a yellow coloration is observed. The γ and δ acetyl derivatives, although very different, since the former is crystalline and the latter amorphous, lead to the same aloins, identical in one case with nataloin and the other with homonataloin. The β derivative is racemic and the other two do not appear to be stereoisomers, but rather different allotropic states of the acetyl derivatives.

MEETINGS FOR THE WEEK.

TUESDAY, 30th.—Royal Institution, 3. "Optical Research and Chemical Progress," by T. Martin Lowry.

THURSDAY, June 1st.—Royal Institution, 3. "Chamber Music and its Revival in England," by Sir Alexander Mackenzie.

Royal Society of Arts, 4.30. "The Work of the Imperial Institute for India," by Prof. W. R. Dunstan.

Royal Society. "Scattering of Plane Electric Waves by Spheres," by Dr. T. J. I'a. Bronwich. "Numerical Results of the Theory of the Diffraction of a Plane Electromagnetic Wave by a Perfectly Conducting Sphere," by J. Proudman, A. T. Doodson, and G. Kennedy. "Motion of Solids in Fluids when the Flow is not Irrotational," by G. I. Taylor.

Chemical, 8. "Hydrates of Aluminium Nitrate," by R. Seligman and P. Williams. "Dyes derived from Phenanthraquinone," by K. C. Mukherjee and E. R. Watson. "Overvoltage Tables—Part I., Cathodic Overvoltages," by E. Newbery.

FRIDAY, 2nd.—Royal Institution, 5.30. "La France dans l'Histoire comme Champion du Droit," by Lieut. Paul H. Loyson.

SATURDAY, 3rd.—Royal Institution, 3. "Folk Lore in the Old Testament," by Prof. Sir James G. Fraser.

ERRATUM.—In the review of "Micro-Photography" (p. 239) Messrs. Campbell, Sons, and Co. were by mistake stated to be the publishers. The author (Mr. George West, University College, Dundee) desires it to be known, to avoid any misunderstanding, that this firm were the printers only, and that all interests or rights in its sale or disposal are retained by himself as author and publisher. (See Advt., May 19).

THE CHEMICAL NEWS.

VOL. CXIII., No. 2949.

THE EFFECT OF UNSATURATION ON THE MOLECULAR VOLUMES OF ORGANIC COMPOUNDS.

By GERVAISE LE BAS, B.Sc. (Lond.).

THIS question, not only as it affects molecular volumes, but also as it affects the physical properties of compounds generally, is always an interesting one, and has received a great deal of attention. The author some time ago (CHEMICAL NEWS, 1914, cx., 27, 37) attempted an analysis of the molecular heats of combustion of hydrocarbons (aliphatic and aromatic), and some interesting regularities were brought to light. It is proposed in this place to do the same for molecular volumes. This paper thus covers the same ground as the former one.

It is now well known that the volume of $H_2 = 7.2$ and that of carbon (C) is 14.5 . The former value is just the difference in volume between an ethenoid compound and the corresponding saturated compound (Table I.).

TABLE I.

	V_m	Δ	V_m	
C_6H_{12} normal hexane	139.9	7.3	132.6	$C_6H_{12} = $
C_3H_7OH	81.3	7.2	74.1	$C_3H_7OH = $
C_3H_7Cl	91.4	7.2	84.2	$C_3H_7OH = $
$(C_3H_7)_2O$	150.9	2×7.2	135.5	$(C_3H_5)_2O$
$CH_3.COOC_3H_7$..	128.5	7.1	121.4	$CH_3.COOC_3H_5$

The same is true of aromatic compounds (Table II.).

TABLE II.

	V_m	Δ
$C_6H_5.CH_2.CH_2.COOH$ (phenyl propionic acid)	170.8	8.1
$C_6H_5.CH:CH.COOH$ (cinnamic acid)	162.7	
$C_6H_5.CH_2.CH_2.COOCH_3$	195.7	7.1
$C_6H_5.CH:CH.COOCH_3$	188.6	

The conclusion is that unsaturation does not produce any effect on molecular volumes, but it is not true without qualification.

1. Double or higher orders of unsaturation (acetylene linkage) or two ethenoid linkages show a slight effect of the nature of an expansion. The examples given in Table III. are taken from the aliphatic and aromatic classes of compounds.

TABLE III.

Compounds.	V_m	Δ	Δ_1
$CH_3.CH_2.CH_2.CH_2.CH_3$	117.8		
$CH_3.CH_2.CH_2.CH:CH$	110.1	7.7	
$CH_3.CH:CH(CH_3).CH_2.CH_3$	117.4		
$CH_2:C(CH_3).CH:CH_2$	103.9	13.5	
$CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$	139.9		
$CH_3.CH_2.CH_2.CH_2.CH:CH_2$	132.6	7.3	
$CH_2:CH.CH_2.CH_2.CH:CH_2$	126.1	6.5	13.8
$C_6H_5.CH_2.CH_3$	139.3		
$C_6H_5.CH:CH_2$	131.5	7.8	
$C_6H_5.C:CH$	126.1	5.4	13.2

The difference for H_2 is about 7.2, but for $2H_2$ 13.5. The expansion is thus $\Delta = 14.8 - 13.5 = +1.3$.

Since $\Delta = H_2$ there is no special effect on volume due to an ethenoid link under the above circumstances. We draw the same conclusion from the following hydrocarbons, which show an interesting constitutive effect:—

$CH_3.CH_2.CH_2.CH_3$ V_m 96.0	V_m 86.9	$\begin{array}{c} CH_2=CH \\ \quad \\ CH_3 \quad CH_3 \end{array}$
$2CH_3$	52.0	
$2CH$	37.0	
	89.0	
Less for $\alpha\beta$ structure ..	-2.0	
ΣV_a	87.0	
V_m	86.9	

Amylene, $CH_3.CH_2.CH_2.CH:CH_2$ V_m 110.1	V_m 108.1	$\begin{array}{c} CH_3 \\ \\ C=CH \\ \quad \\ CH_3 \quad CH_3 \end{array}$
	Δ -2.0 for $\alpha\beta$ structure.	

$\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ CH-CH \\ \quad \\ CH_3 \quad CH_3 \end{array}$ V_m 136.8	Δ 7.6	V_m 129.2	$\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ C=C \\ \quad \\ CH_3 \quad CH_3 \end{array}$
$4CH_3$		104	
$2C$		29.6	
		133.6	
Less for $\alpha\beta$ structure ..		-4.0 (2×2.0)	
ΣV_a		129.6	

The series given in Table IV. is instructive as showing a similar effect when a relatively small atom like chlorine is replaced by larger ones like bromine or iodine—that is, the presence of substituents like Br and I have the effect of expanding the volume in a similar way to the second elimination of H_2 in the hydrocarbons.

TABLE IV.

Compound.	V_m	Δ	B.-p.
$\{CH_3.CH_2.CH_2Cl$	91.4		44
$\{CH_2:CH.CH_2Cl$	84.2	7.2	46
$\{CH:C.CH_2Cl$	77.7	13.7 (2×6.85)	65
$\{CH_3.CH_2.CH_2Br$	97.4		71
$\{CH_2:CH.CH_2Br$	90.5	6.9	71
$\{CH:C.CH_2Br$	84.1	13.3 (2×6.65)	89
(mean)			
$\{CH_3.CH_2.CH_2I$	106.9		102
$\{CH_2:CH.CH_2I$	101.2	5.7	101
$\{CH:C.CH_2I$	94.6	12.3 (2×6.15)	115

The effect depends partly on the nature of the halogen atom and partly on the degree of unsaturation.

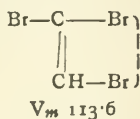
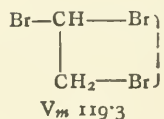
In the case of the vinyl compounds the bromine atom or atoms are capable of producing effects which are similar to those shown above.

$\begin{array}{c} CH_2-Br \\ \\ CH_2-Br \end{array}$ V_m 97.1	Δ 5.7	$\begin{array}{c} CH-Br \\ \\ CH-Br \end{array}$ V_m 91.4
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2CH ₂	44.2	2CH	37.0
2Br	56.0	2Br	56.0
	100.2		93.0
Less for αβ structure	-3.1	Less for αβ structure	-3.1
Σ _n V _a	97.1	Σ _n V _a	89.9
V _m	97.1	V _m	91.4

Augmentation for unsaturation .. +1.5

$$\Delta = 7.2 - 1.5 = 5.7.$$



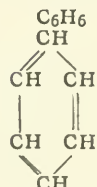
$$\Delta \ 5.7$$

The conclusion is that among aliphatic or open-chain compounds single and double unsaturation produces but little effect on the volume at the boiling-point.

A final example of this constitutive feature is to be found in the alkyl and alkylene salts of the fatty acids.

Unsaturated Rings.

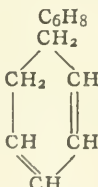
A study of the benzene and hexahydrobenzene nuclei has already been made, but additional facts have recently come to light, which have an important bearing on the question of the constitution of those nuclei. It has already been shown (CHEMICAL NEWS, 1908, xcvi., 85; 1909, xcix., 206) that so far as the volume at the boiling-point is concerned, six of the hydrogen atoms of hexamethylene possess an aromatic character, but that the six *extra* hydrogen atoms are truly paraffinoid. It must be remembered that we are comparing these substances at the boiling-point.



Benzene.

C=0.45
B.p. 80.5
V_m 96.0

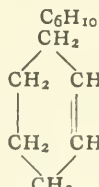
$$\Delta \text{ for H}_2 \ 6.0$$



Dihydrobenzene.

V₂₀ 94.3
B.p. 85
102.0

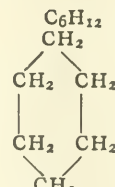
$$7.1$$



Tetrahydrobenzene.

V₂₀ 101.2
B.p. 83
109.1

$$7.2$$



Hexahydrobenzene.

B.p. 79
116.3

Moreover,—

Hexylene, C₆H₁₂—Hexamethylene, C₆H₁₂ = 131.4—116.3 = 15.1 for ring structure.

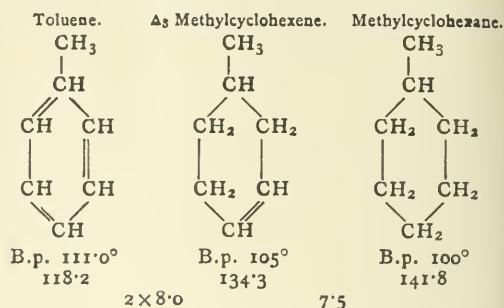
The above evidence is conclusive that as we pass from benzene to hexamethylene by steps, we produce two and one ethenoid links which resemble those in the open-chain olefins, because the hydrogen atoms possess precisely the same values as in those compounds. The resemblance between the two series is rendered more prominent from the fact that the first difference is only 6.0. This agrees with the rule for the effect of two ethenoid links on the value of Δ. It follows that the extra hydrogens in the reduction products of benzene resemble those in the paraffins, but that the remaining six are aromatic in character; that is, so far as their effect on the volume is concerned.

As regards benzene, we suppose that carbon and hydrogen maintain their relative volumes, but actually are less than their values in the paraffins. This occasions a contraction for ring structure. The nucleus C₆H₆ remains in the reduction products of benzene, both as regards actual

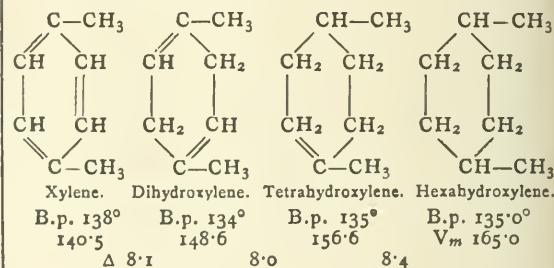
volume and the immediate cause of the contractions which affect all these compounds.

C₆H₆, C₆H₆.H₂, C₆H₆.H₄, C₆H₆.H₆.

At the critical point the distinction as regards volumes of hydrogen is lost in benzene and hexamethylene. In both compounds V/W=8.5; that is, H=8.5 and C=34.0. This shows that the critical and boiling-points are somewhat different in regard to their evidence for structure.



The evidence furnished by this series is not quite so clear as in the foregoing case, but we see that the difference for H₂ is about the same value as before. If anything there is an increase in the apparent value of H₂, due probably to the paraffinoid radicle CH.



It is quite clear that the volumes of H₂ are equal to 8.0 or H = 4.0. This increase may be regarded as due to the influence of the paraffinoid residues.

Owing to their importance, we give in Table V. the corresponding results for the derivatives of cymene.

C=0.53.		TABLE V.		
Cymene—	B.p.	d.	V.	
C ₃ H ₇ .C ₆ H ₄ .CH ₃ ..	175°		184.6	
		Δ(H ₂)	6.1	
Carvene—				
C ₃ H ₅ .C ₆ H ₄ .H ₄ .CH ₃	176°		(190.7)	
Menthene—				
C ₃ H ₇ .C ₆ H ₄ .H ₄ .CH ₃	167°	d ₁₅ 0.815	200.5	
		Cymene	184.6	
			15.9 for 2H ₂	
			(7.95)	
		Δ(H ₂)	8.0	
Hexahydrocymene—				
C ₃ H ₇ .C ₆ H ₄ .H ₆ .CH ₃	158°	d ₀ 0.802	208.5	
		Cymene	184.6	
			23.9 for 3H ₂	
			(7.97)	

The value for carvene is out of harmony with the other results, and with it all the other terpenes which possess volumes of from 189.5—191.0, because the difference for H₂ is the usual one. The boiling-points of carvene and cymene are similar. The hydrogen atoms resemble those

of dihydro-benzene so far as their volumes are concerned. In all these other reduced nuclei, six of the hydrogen atoms resemble those of benzene, and the remainder are paraffinoid. The paraffinoid character of the extra hydrogens is enhanced by substitution of the nucleus by alkyl residues.

The naphthalene reduction products behave similarly. This is remarkable since it shows that the second ring acts like a paraffinoid substituent.

We see the above evidence is of a striking and complete character, bearing out the original hypothesis regarding the influence of the structural relations of the compounds and their molecular volumes.

THE NATIONAL WASTE OF TOBACCO ASH.

By B. A. BURRELL, F.I.C.

THE present war has taught the country at large and chemists in particular many much needed lessons, and we are now realising how dependent we had become on Germany for our dyes, glass, porcelain, and many chemicals, including potash.

As regards the latter there is no particular credit due to German genius except for the careful and systematic method in which they have utilised the immense natural deposits of potash salts which occur at Stassfurt. These had given to Germany a world monopoly with which it was impossible to compete with our present system of free imports.

The following figures, taken from the "World's Supply of Potash," published by the Imperial Institute, give the value of the potash salts imported into the United Kingdom during the years—

	1912.	1913.
Foreign nitrate of potash (excluding Indian)	£172,946	£184,335
Other foreign potash salts	£614,077	£625,834

—the great bulk of the foreign nitrate and other potash salts being from Germany.

Excluding the German deposits, the only one of any magnitude in Europe is that recently discovered at Cardona, in Catalonia, which appears to be of great promise but requires development, and it will probably be some time before it can be regarded as a source of supply.

Before the discovery of potash in the Stassfurt deposits about the year 1857 we had derived our potash from such sources as marine plants, sea water, wood, wool washings, &c.

About 90 per cent of the imported potash is used in agriculture.

Before the war artificial corn, potato, and turnip manures generally contained potash salts equivalent to about 5 per cent of potash. The universal shortage was making itself felt early in 1915, with the result that the quantity of potash in this class of manures was being much reduced, and in many instances they are now being sold as containing no potash.

At that time Fairley and I received a number of samples of wood ashes from farmers in various parts of the North of England to be examined for the quantity of potash contained therein. Some of these had obviously been mixed with much earthy matter, the potash only being about 2 per cent, in others it reached 11 per cent, or nearly as much as in kainit, which generally contains about 12½ per cent.

Kainit at that time was being sold at £6 2s. 6d. per ton, whereas at the corresponding period of 1914 it only cost £2 7s. 6d. per ton. Now it is not obtainable.

The *Journal of the Board of Agriculture*, 1914, xxi., 694, contained an article by Dr. Russell, showing that the ashes of threshing waste, grass, weeds, dead and green wood contained about 11 per cent of potash.

A short time ago the Imperial Institute issued the very

useful pamphlet "The World's Supply of Potash," in response to numerous inquiries respecting new sources of supply.

It is well known that all parts of the tobacco plant are rich in potash. In America the stems and waste from the factories are already being utilised.

The portion used for smoking is the leaf, and it may be stated that in round numbers the ash (including unburnt tobacco) from a pipe, cigar, or cigarette is about 30 per cent, and that one-fifth of this, or 6 per cent, is potash; or in 100 parts of ash there are potash salts equivalent to 20 parts of potash.

Tobacco ash is thus extremely rich in potash. It may be regarded as the by-product in the operation of smoking, and at the present time this valuable by-product is being completely wasted, whereas by a little organisation a great deal of it might be saved and used as a source of potash. Tobacco ash also contains another fertilising ingredient, viz., phosphoric acid, to the extent of about 5—6 per cent.

It is I think a matter of common agreement that as a nation we shall in the future have to practise the most rigid economy, and that we must try to reduce our imports as much as possible. One of the imports that could be reduced or stopped are the German potash salts.

We have commenced to make our own dyes, chemical and optical glass, porcelain, and filter papers: then why not try to be independent of German potash and stop the daily waste of potash in tobacco ash and household vegetable refuse. The latter does not, however, come within the scope of this note.

By the systematic collection of tobacco ash from pipe tobacco, cigars, and cigarettes, hotel and restaurant keepers would be doing a national service and at the same time add to their incomes. I would suggest that every hotel, restaurant, and publichouse should have its tobacco-ash tub, into which tobacco-ash trays from the smoke-room, &c., should be emptied, and that they form a combination for its collection and sale to the artificial manure maker or the manufacturing chemist.

The material is there; in any case it has to be collected; but instead of throwing it away, as at present, it should be utilised.

Every district should have its potash recovery department, which should work up not only tobacco ash but household vegetable refuse and vegetable waste from the markets and greengrocers' shops. Such a scheme would help to provide employment for our own people and to materially lessen our imports.

In order to put the matter as fairly as possible the following illustrations are given:—

An ordinary sized cigar will measure about 4½ inches by half an inch, and will weigh about 106·5 grains. If carefully smoked it will take about one hour to burn and will give about 32·3 grains of ash, of which one-fifth, or 6·5 grains, is potash.

An ordinary sized cigarette will weigh about 27 grains, will take about twenty minutes to burn, and will give about 8·5 grains of ash, of which one-fifth, or 1·75 grains, is potash.

An ordinary sized pipe will hold about 25·5 grains of tobacco, will burn for about twenty minutes, and will give about 8·0 grains of ash, of which one-fifth, or 1·60 grains, is potash.

Now take some results of systematic collecting:—

1. Tobacco ash and unburnt tobacco from the smoke-room of a club, collected for eight days, weighed 9½ ounces.
2. From the lounge of a large hotel, collected for four days, weighed 13 ounces.
3. From a large restaurant, collected for ten days, weighed 2 lbs. 8 ozs.
4. From a music hall, one-tenth part of the auditorium, one performance only, weighed four ounces.

If it is remembered that this ash is being produced all over the country day by day we can begin to appreciate the quantity of valuable matter that is being wasted.

By the kindness of Mr. Murgatroyd, of Messrs. Hardy and Co., tobacco and cigar importers, I am enabled to give the actual amount of tobacco and cigars consumed in the United Kingdom for one year, March 31, 1913, to March 31, 1914. Tobacco was 98,412,412 lbs., the total population being 46,407,037, or an average consumption per head of the population of 2·08 lbs. During the same period the imported cigars consumed weighed 1,331,802 lbs.

I have converted Mr. Murgatroyd's figures into tons, so as to be more easily grasped. The total consumption of tobacco and cigars in tons comes to (in round numbers) 44,529. This when burnt will give 13,359 tons of ash. If we assume that the ash contains one-fifth of its weight of potash (which is a low estimate) we get 2672 tons of potash, and as kainit only contains 12·5 per cent of potash we may say that we are annually throwing away potash equivalent to 21,376 tons of kainit. In the spring of 1914 the cash price of kainit at Goole was £2 7s. 6d. per ton, so that this quantity of kainit would be worth nearly £51,000. In the spring of 1915 it was worth nearly three times as much.

From these figures there would, of course, have to be considerable reductions for unavoidable wastage.

ANALYSIS OF NIOBIUM-TITANIUM MINERALS, WITH SOME NEW TESTS FOR NIOBIUM, TANTALUM, AND TITANIUM.

By JAMES MOIR, M.A., D.Sc.

THE following modification is an improvement on the known process for separating the constituents of euxenite, æschynite, pyrochlore, and similar minerals—namely, those which contain titanium in addition to niobium and tantalum.

The agated specimen is fused with caustic potash (not soda) and the melt dissolved in twenty parts of water and immediately filtered through a hardened paper in a Buchner funnel under reduced pressure, finally washing out the insoluble matter with warm dilute potassium hydrate solution. By this method practically all the titanium remains behind "salted out" as K_2TiO_3 along with the true insolubles (the hydrates of iron and manganese and the yttrium and didymium earths), whereas in Simpson's process (Geological Survey Bulletin, Western Australia, 1906) the solution is acidified, thus bringing the titanium into solution, in which case, according to my experience, it cannot be separated from niobium—at least within 5 or 10 per cent of the true value. The use of caustic potash in the fusion is essential, since sodium titanate does not "salt out" satisfactorily and tends to redissolve on attempting to wash it. In addition, sodium tantalate is so sparingly soluble compared with potassium tantalate that tantalum may be overlooked from being left in the "insolubles." The alkaline filtrate may contain silicate, tantalate, niobate, stannate, and manganate as potassium salts. For identification of Nb and Ta it is then treated with strong sodium hydrate solution, when sodium tantalate if present crystallises out in needles in the course of a minute, and on decanting the supernatant liquid and allowing to stand for several hours sodium niobate crystallises out in hexagonal plates. This method does not profess to be quantitative, but it affords a remarkably decisive identification of these troublesome elements.

Reactions of Niobic Acid.—Solution of sodium niobate when treated with acid not in excess and warmed is precipitated as hydrated niobic acid, but if rapidly mixed with excess of cold HCl gives a clear solution, and it is only with such a clear solution that the confirmatory tests for niobium can be got. The precipitated niobic acid is also fairly soluble in hot strong hydrochloric acid (concentrated acid plus half its bulk of water), and this solution gives

most of the subjoined tests. Curiously enough $HNbO_3$ is much less soluble in concentrated HCl than in the above mixture.

The following are some of the known tests for niobium, including both the ancient and the modern; the clear solution of $HNbO_3$ in HCl is used.

(1). **Tannin Test.**—Pure niobic acid gives a reddish chocolate precipitate, whilst pure tantalac acid gives a sulphur-yellow precipitate; the usual colour with crude niobates containing tantalum is russet brown.

(2). **Ferrocyanide Test.**—Complete absence of iron is naturally necessary. $HNbO_3$ gives a red brown precipitate (like that of uranyl salts). $HTaO_3$ gives nothing in the cold and a yellow precipitate on warming.

(3). **Nascent Hydrogen Test.**—Addition of zinc to the acid solution of $HNbO_3$ gives a brown colour if the acid is strong and the action vigorous; if the acid is weak an intermediate olive coloration is observed. If both titanium and niobium are present the colour is indigo blue, probably a combination of the violet of titanium with the olive colour of niobium. If tungsten is present a deep indigo-coloured precipitate (not coloration) is produced.

(4). **Meimberg's Tin Test.**—The solution of $HNbO_3$ in strong (2 : 1) HCl is boiled with tin for some time, when a deep sapphire-blue coloration is obtained, fading on standing and regenerated by boiling. This is the most sensitive test for niobium. Note the remarkable difference in the behaviour of zinc and tin in niobium solutions.

(5). **Pennington's Sulphocyanide Test.**—An alkaline niobate solution treated first with sulphocyanide and then acidified gives a yellow coloration; then on adding zinc the solution becomes greenish and finally red-brown (*Journ. Am. Chem. Soc.*, 1896, p. 51). This also is a sensitive and characteristic test.

The following are some new reactions observed by the writer:—

(1). $NaNbO_3$ treated with ammonium oxalate and then with acid and zinc gives a deep brown coloration, not altered by hydrogen peroxide or by sulphocyanide. On prolonged reduction the colour fades to yellow. Titanium solutions treated in this way give a dull yellow colour, changing to orange-red with hydrogen peroxide.

(2). $NaNbO_3$ treated with Rochelle salt or other tartrate and then with acid and zinc gives a permanent brown solution.

(3). Potassium hydrosulphite (from zinc dust and potassium metabisulphite) added to an acid solution of niobic acid gives a curdy yellow precipitate, oxidising on standing to white niobic acid. Titanium solutions with this reagent give a red orange colour very similar to that given by the H_2O_2 test for Ti. The violet colour of trivalent Ti could not be observed as an intermediate stage.

(4). Pyrogallol (and other polyhydroxybenzenes and allied substances such as gallic acid) give an orange precipitate with niobic acid, but mineral acid must not be present in excess; this is analogous to the known tannin test, but the colour is more characteristic and less liable to be confused with that from titanium. Tantalum gives pale yellow precipitates with these reagents.

(5). **Reactions of Niobium and Tantalum in Concentrated Sulphuric Acid.**—If a few mgrms. of $NaNbO_3$ or $NaTaO_3$ are added to concentrated sulphuric acid and the latter gently boiled for a minute a clear solution is obtained. Tantalac acid dissolves comparatively slowly and generally leaves a faint opalescence. The solution on cooling is treated with various phenolic bodies, and gives characteristic colour reactions in the case of niobium, but only yellow colours in the case of tantalum. The test is analogous to the thymol test for titanium and gives a somewhat similar range of colours (Lenher and Crawford, *Journ. Am. Chem. Soc.*, 1913, p. 138, and Report of 1912 International Congress). Niobium may be confirmed in presence of titanium by subsequently diluting with four parts of water and adding zinc, when a further series of reduction-colours is given by niobium, whereas titanium

gives a barely visible violet coloration and tantalum gives no reduction-colour. Thus thymol, hydroquinone, pyrogallol, and pyrocatechol give blood-red colorations with niobium in concentrated H_2SO_4 , which on dilution and treatment with zinc give inky greenish reduction colours, whilst phenol at first gives an orange, which on dilution and reduction gives a dirty violet, and morphine gives a pink, going yellowish green on reduction.

Tests for Titanium.—The most sensitive is Lenher and Crawford's, mentioned above, viz., a solution of thymol in sulphuric acid added to the titanium compound, dissolved either in concentrated H_2SO_4 or by fusion with KHSO_4 , diluting with concentrated H_2SO_4 . The coloration is garnet red and the test is twenty times as sensitive as the hydrogen-peroxide test.

The writer has noticed that the violet reduction colour of titanium is much intensified by adding sulphocyanide after reducing with zinc and hydrochloric acid. Under these circumstances the colour is as intense as that given by the H_2O_2 test and is not given by any other metal.—*Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, xvi., No. 8.

LUTES AND CEMENTS.*

MATERIALS OF VALUE TO THE CHEMIST, PHYSICIST,
AND EXPERIMENTER.

By S. S. SADTLER.

I USE the words *lutes* and *cements* together for two reasons. First, because they have different meanings, the former referring to temporary applications, and the latter to more permanent uses. Second, the use of these words conjointly shows to a casual reader that the subject of this paper is not solely with reference to Portland cement.

Quite a few years ago I read several papers on the present subject. In these papers I classified the formulæ according to composition in one instance and according to intended use in another. These papers were noticed by a number of people who communicated with me, particularly engineers.

It is very difficult to give proper credit for what one finds in the literature, as some of these formulæ are like humorous stories that are rarely traceable to a source. In looking up this subject for the present occasion I noticed some eight or ten attractive formulæ in a well-known handbook of industrial chemistry. These were credited to a periodical which I soon found quoted in one of my papers, and I was not the originator of more than a few of them. Thus, things are passed on. The value of the formulæ was diminished, however, by reason of the space allotted and the changes made.

I will classify the formulæ now as I did before the Engineers' Club of Philadelphia, by the use of the following sub-divisions. Very few of the formulæ given herewith have not been tried by me. The only instances are where the authority was excellent, and adequate trial was not practicable for some reason.

Waterproofing.—Of the chief bituminous substances available we have pitches, asphalts, gilsonite, and blown petroleum residues, mixtures of these substances, and mixtures of the same with inert material.

(a) Of the asphalts I prefer a substance like refined Bermudez, as it is nearly pure bitumen, and forms homogeneous solutions with suitable solvents. A minor percentage of boiled linseed oil or blown petroleum oil is useful sometimes for tempering or fluxing. For solvents heavy naphtha is generally used. It does not dissolve all the asphalt, such as the so-called asphaltene portion, but it thins out the asphalt well enough. Coal-tar naphtha

is better but more costly. As voids are very apt to form in a painted asphalt coating, some form of filler is generally employed, either by coating paper so that it becomes more or less impregnated or by the addition of a filler, such as silex, infusorial earth, &c. The natural mineral filler of Trinidad asphalt may serve the purpose of such filler.

(b) For a soft water-tight coating in cement work, blown asphalt and infusorial earth, thinned with a solvent, such as heavy naphtha, is employed.

(c) The use of blown asphalts with natural asphalts and gilsonite is in some cases desirable, as these products are ideal fluxes for hard asphalts, and tend to prevent brittleness or separation of the films when the solvent evaporates. The harder or higher melting-point grades of these blown residuums are capable of making good cements alone or with filler, but are rather hard to dissolve. Such artificial asphalts have melting-points as high as 150°C ., while the softer ones that are probably best for fluxing have melting-points about 80°C .

(d) Lutes of boiled linseed oil, thickened with clay, asbestos, red or white lead, &c., are waterproof, if thick enough from the filler added.

(e) Flax-seed meal made into a stiff paste with water is useful as a lute for steam connection and is easily applied.

Portland cement only serves as a waterproof cement when given time for the preliminary setting to take place. It is not generally impervious to water, and because of its colloidal character while setting it seems hard to realise that it could ever act other than as a water pervious diaphragm. But when fully or reasonably well set and dry the colloid character no longer exists, and does not return to these particles that have taken part in the setting from hydration.

For all practical purposes the use of trade preparations, such as those containing metallic soaps or oil emulsions, serves to render concrete approximately impervious, but I will refer to a few points I have noticed in making or using lutes and cements.

(f) For making small experimental electrolytic cells, &c., for demonstration purposes, I have found it desirable to use white iron-free Portland cement and white plasterers' sand that had been sieved. If a one-to-two mixture is made with the prescribed quantity of an approved waterproofing substance, such as the product of the Newberry patent, and care is taken to work out voids and the article in the green is kept moist, a very nice waterproof container can be made. It will also stand dilute acids or alkalis, but not the two alternately. For large articles wire-mesh reinforcement is often desirable, and if the vessel is used for dilute acids this might well be made of a mesh of Monel metals, &c.

(g) In the literature on this subject, if it can be dignified by that appellation, one finds frequent reference to making lutes with Portland cement and silicate of soda. Some of these may work and others will not, and I approach them with caution. A little silicate of soda in the water will help toward a quick initial set, for instance, for under-water work. Water containing 4 to 20 per cent of silicate of soda by volume causes a preliminary set in two hours that prevents washing away by water. It injuriously affects the natural and gradual hydration, however, unless the sodium hydroxide, carbonate, or sulphate is washed out by excess of water, which is difficult to do. Mixtures containing above 4 per cent of silicate show strong efflorescence, which is particularly marked with that made with 20 per cent aqueous solution of silicate. The silicate of soda setting is at first due purely to double decomposition of sodium silicate and calcium hydroxide. If very strong silicate is used the mass stiffens so fast that it cannot be worked. This is true of all concentrations of 50 per cent or over.

There is one point that might be noted. For immediate immersion in running water silicate of soda acts as a binder, while the particles of the cement form gelatinous

* A paper read at the Baltimore Meeting of the American Institute of Chemical Engineers. From the *Scientific American Supplement*, lxxxi., No. 2104.

colloids instead of being washed away. The soluble sodium salts are more or less eliminated, and apparently normal concrete results. I have used glue solutions (3 to 5 per cent strength) with white Portland cement to secure very dense compositions. It is possible that the glue aids colloid formation, and protects the same against too rapid crystallisation.

Oil Proof.—(a) Several of the best known lutes I am placing under this category, although they might be classified elsewhere:—

Good glue	2 parts by weight
Glycerin	1 " "
Water	7 " "

The glue is first softened by the water, then liquefied by heat, and the glycerin incorporated. This is a good lute to render corks vacuum tight, for stopping small leaks of almost anything except water and steam.

(b) The following has been found useful in laboratories and in the works for oil vapours:—

Putty of molasses and flour.

(c) The next lute to be mentioned is one of the best known and most useful. The proportions given are those I have found satisfactory:—

Glycerin	90 parts by volume
Water	10 " "

To be made into a stiff putty with—

Litharge	90 parts by weight
Red lead	10 " "

It takes several hours to stiffen and about a day to set.

(d) Several cements of which silica of soda is an active principle or the chief binding substance are as follows:—

Silicate of soda (about 30° Bé.).
Whiting.

Made into a stiff putty.

This slowly sets by drying if not by chemical action. If magnesium carbonate be used the setting is so quick that it is hard to use the mixture. If it is used, however, the silicate should be diluted to one-third to one-half normal strength. I do not recommend either of them.

(e) Barium sulphate is often used with silicate of soda. The silicate should be about 30° Bé. If the mixture is heated by a preliminary heating of the silicate or it is put into a hot place there seems to be some chemical reaction which aids in the setting.

(f) A very strong and ultimately hard cement or substance for a variety of purposes is made by incorporating glue with plaster of paris. This will be described with other plaster plastics in Section 6.

Acid Proof.—(a) The asphaltic preparations referred to in Section 1 are largely acid proof. Black putty, the formula for which was first noticed by me in a "Handbook of Chemical Engineering," by George E. Davis, is made by intimately mixing equal weights of china clay, linseed oil, and gas-tar. The ingredients must be anhydrous, so it would probably be best to take a tar residuum or very soft pitch of thick, so-called, creosote oil. Rubber cements may have varied composition, but I will only refer to two which are, perhaps, extremes. If equal parts of fresh unvulcanised rubber are used the mass is so stiff that it would be probably used alone. If as much as four parts of linseed are used considerable filler can be incorporated and make a workable putty.

(b) Equal weights of rubber and boiled oil are taken; the rubber is first dissolved in carbon disulphide in the proportion of 4 cc. carbon disulphide to 1 grm. of cut-up rubber. Boiled linseed oil is then mixed in, and the mixing is facilitated if the oil is warm. The solvent is generally not removed by evaporation until the paste is applied.

(c) The other formula, to which reference has just been made, differs in having four times as much boiled linseed oil, and then fire clay or other filler, such as silex, is used.

Crude, finely cut rubber ..	1 part by weight
Linseed oil, boiled	4 " "
Fire clay	6 " "

(d) Melted sulphur with fillers of stone powder cement, sand, &c., are used. The following is used for hydrochloric acid vapours:—

Rosin	1 part by weight
Sulphur	1 " "
Fire clay	2 " "

Linseed oil (boiled) and fire clay stand most acid vapours.

(e) According to Davis red lead and litharge in boiled oil stand acid vapours (even nitric acid).

Litharge	80 pounds
Red lead	8 " "
Flock asbestos	10 " "

Fed into a mixer, a little at a time, with 6 quarts of boiled linseed oil.

There are numerous acid resisting mixtures possible in which silicate of soda is used. This is possible, in spite of the strong basic character of silicate of soda, because the silicate is superficially changed to colloidal silica, which continues the cementing work, at first effected by the silicate of soda.

(f) Barium sulphate, powdered glass, china clay, &c., are used with silicate of soda slightly diluted with water. A strength of about 30° Bé. is close to what is best for the purpose.

(g) The following I have used with success for dilute hydrochloric acid:—

White china clay	1 part by volume
Fine white sand, or powdered quartz and sand	2 " "

are mixed thoroughly, and worked up with just enough silicate of soda, diluted with an equal volume of water to make a paste. This can be rendered more impervious to water by the judicious incorporation of organic colloids. If a little fine casein be incorporated with the silicate of soda in a mixer so that the mixture is quite smooth the mass will be better. About 5 per cent of fine dry casein powder is added, based on the weight of silicate. If fresh milk curd can be used, corresponding to the same dry weight of casein, and allowance is made for the water contained, a mechanical mixer may not be needed.

Chlorine Resistant.—(a) The most reliable are made with Portland cement as chief ingredient:—

Powdered glass	1 part
Portland cement	1 " "
Silicate of soda	1 " "

The last mentioned should be diluted considerably so as not to set too fast.

Portland cement quickly reacts with silicate of soda, but powdered glass and clay react more slowly with silicate of soda, but finally render the cement insoluble as regards its mass.

General Purposes with Plaster of Paris.—This series of lutes and cements is highly important, and individual formulæ will serve to prevent the escape of hydrocarbon and other gases in furnace work, as cements for mechanical purposes, and as coatings, such as plaster, when mixed with asbestos straw plush trimmings, hair, &c.

(a) Soluble sulphates form double sulphates with calcium sulphate and with water. They set harder and are more impervious than calcium sulphate (plaster of paris) alone. It is desirable not to take equal molecular quantities to form the full double sulphates, but about half of these quantities. Sodium, potassium, and aluminium sulphates are used for this purpose.

(b) According to Sigmund Lehner, a little borax in the water used makes hard cements, and regulates the setting: 12 volumes water to 1 volume saturated borax solution sets in fifteen to twenty minutes at 10° C.; 8 volumes

water to 1 volume saturated borax solution sets in one hour. The same author gives a formula credited to Viotti for a weatherproof plaster cement.

(c) 1500 grms. of borax and 150 grms. of magnesium oxide are melted together and powdered. This powder is then mixed with 75 grms. of plaster of paris. Borate of magnesium thus predominates and protects the plaster from being washed away by water.

Marine Glue.—Standard preparation of this class of lutes (which are applied to crevices, &c., hot, and get firm but not brittle when cold) is composed as follows:—

Crude rubber		1 part by weight
Shellac		2 " "
Pitch		3 " "

The rubber is first dissolved in carbon disulphide or turpentine before mixing with the heated (not superheated) mixture of the other two. The advent of blown petroleum residuums has made it possible to make up hard but flexible compounds without rubber. Grahamite is a good base to which fluxes, such as these just mentioned or soft asphalts, are added.

Gasket Compositions.—There are so many good gasket compositions on the market that I was on the point of omitting all reference to them. For factory work I have found no trouble in getting ropes of graphitised asbestos, rubber composition, leather fibres cemented with rubber, &c., that are quite satisfactory.

In the laboratory one can generally make out for low temperatures and pressures by saturating heavy "kraft" wrapping paper with soft pitch, such as wood pitch for steam, or with gelatin and glue (hektograph) composition for oils. For high pressures, slots filled with lead rings and a V-shaped rim to the lead are most satisfactory.

Machinists' Cement.—A few words might be said here with reference to machinists' cement. These are the well-known red and white leads. The red lead is often diluted with an equal bulk of silica or other inert substance so as to make it less powdery on drying. The best way that I have found to accomplish this, however, is to add rubber or guttapercha to the oil as follows:—

Linseed oil		6 parts by weight
Rubber or guttapercha		1 " "

The rubber or guttapercha is dissolved in sufficient carbon disulphide to give it the consistency of molasses, mixed with the oil, and left exposed to the air for about twenty-four hours. The red lead is then mixed to a putty. Oxide of iron makes less brittle cements than red lead.

Leather Cement.—As cements of this class are apt to be wanted by chemists sometimes, I quote from my paper in the *Transactions of the Engineers' Club of Philadelphia* (1904, xxi., 4).

The following formulæ are given in the *Papier Zeitung* (xviii., 2618):—

"(a) Equal parts of good hide-glue and American isinglass, softened in water for ten hours, and then boiled with pure tannin until the whole mass is sticky. The surface of the joint should be roughened and the cement applied hot.

"(b) One kilo. of finely shredded guttapercha digested over a water-bath with 10 kilos. of benzol, until dissolved, and 12 kilos. of linseed oil varnish stirred in.

"(c) Seven and one-half kilos. of finely shredded india-rubber are completely dissolved in 10 kilos. of carbon disulphide by treating while hot, 1 kilo. of shellac and 1 kilo. of turpentine are added, and the hot solution heated until the two latter ingredients are also dissolved." Precautions against fire and vapours should be observed.

(d) Another one noticed in the *Journal of the Society of Chemical Industry*:—

Guttapercha		8 ounces
Pitch		1 " "
Shellac		1 " "
Olive oil		1 " "

These are melted together.

Iron Cements.—When iron in a fine state of division, as in fresh oil-free filings or cast-iron borings that have been powdered, is mixed with an oxidising agent, such as manganese dioxide or a substance electro-negative to iron such as sulphur, in a good conducting solution like salt or salammoniac, galvanic action sets in very rapidly, ammonia is given off (if salammoniac be used), and the iron swells, by forming iron oxide, and cements the mass together. It is best diluted with Portland cement. A formula which I give from memory is:—

Iron filings		40 parts
Manganese dioxide, or flowers of sulphur		10 "
Salammoniac		1 "
Portland cement		20 to 40 "
Water to form a paste.		

These cements are used extensively in foundries, &c.

I prefer manganese dioxide to sulphur as a negative element. The free carbon of cast-iron that has been powdered is negative pole enough to react, but the use of manganese dioxide causes quicker action. If not diluted with cement they are apt to expand too much and bulge out from the hole or crevice in the iron.

Crucible Cements.—(a) Mixtures of clay and borax in which the clay predominates. Silicate of soda and powdered glass or sand are the best known compounds for cementing lids on crucibles, &c. Sometimes the "iron cements" are used for such purposes, or iron filings and a little manganese dioxide are added to the above compositions for crucible cements.

(b) Probably the best known cement for graphite is fire clay, which with water binds the graphite fairly well and itself stands high temperatures.

(c) In some cases it is desirable to have an all-carbon binder, and for this purpose tars or soft pitches are used. Very little binder must be used, however, or the material will crack when heated, as the carbonising of the pitch shrinks the binder somewhat. Starch paste has been recommended for this purpose, but the shrinkage is greater and the binding is not as good.

(d) A strong waterproof cement that will stand high temperatures may be made by mixing powdered silica or fine sand and powdered silica with a solution of magnesium chloride of about 10 per cent strength. This composition is applied as a putty, and then painted or soaked in a solution of silicate of soda of about 30 per cent strength. This forms magnesium silicate as a binding material for silica.

Magnesia Composition for Furnaces, &c.—Magnesia burned at incandescent heat or hard-burned, 80 per cent. Magnesia light-burned (just sufficient to drive off carbon dioxide, dull redness), 20 per cent. The composition is made into a stiff putty with water, and shaped as desired. The water must be driven off very slowly. A small proportion of good asbestos fibre may be worked in to keep from cracking.

Oxy-chloride Cements.—These are sometimes called stone cements, and the only one of practical importance is that made with magnesium chloride.

If the magnesium chloride is quite pure, i.e., free from potassium or calcium chloride, the solution used need not be more than 18° Bé., but if commercial German magnesium chloride be used it requires a solution of 20° to 22° Bé. The magnesium oxide must be freshly burned at a dull red heat, as the light oxide that is requisite for this cement readily absorbs carbon dioxide from the air and becomes unsatisfactory or of no use for making cement compositions. A diluent for the magnesium oxide is generally used, such as silica or wood-pulp, ground wood, &c.

This communication is not offered as being an exhaustive treatment of the subject, but as an attempt at bringing together only tried or traceable formulæ for the making and using of lutes and cements.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 18, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"An Active Modification of Nitrogen." By Hon. R. J. STRUTT, F.R.S.

1. The production of active nitrogen in various regions of the steady discharge has been studied. It is greatest near the cathode, falls off to a minimum in the Faraday dark space, and increases again in the positive column to a value which is constant along that column, but less than that at the cathode.

2. With a given value of the current much more active nitrogen is obtained from the positive column in a narrow tube than in a wide one. The difference between the potential gradients in the narrow and wide tubes is not large enough to plausibly account for the different yield of active nitrogen, which must rather be connected with the current density.

3. The yield of active nitrogen comes to a limit as the length of positive column traversed by the gas is increased. This is shown to be due to a destructive action of the discharge, which beyond a certain concentration destroys the active nitrogen as fast as it is produced.

4. A trace of oxygen (or almost any other admixture) is known to greatly increase the yield of active nitrogen. The amount of oxygen required to do this considerably increases the fall of potential at the cathode, but it does not measurably affect the fall of potential in the positive column.

5. Active nitrogen is produced by the spark at atmospheric pressure. That the phenomena are so much less striking than at low pressures is due to the destructive action of the surrounding gas on the active nitrogen after it is produced.

6. The metal scattered from a copper cathode when the discharge passes can be made to emit its line spectrum in a stream of active nitrogen.

"A Theory of Colour Vision." By R. A. HOUSTON, D.Sc.

The paper explains the facts of colour-mixing by assuming the existence of one class of oscillators in the retina with a free period in the middle of the spectrum. Owing to disturbing influences the vibrations of these oscillators are never monochromatic, but when represented by a Fourier integral contain a range of wavelengths. Thus, even if the incident light is pure red or pure green, the vibrations contain yellow as well. Hence if the vibrations of the oscillators are identified with subjective light simultaneous excitation of the eye with red and green produces yellow.

"Linkages Illustrating the Cubic Transformation of Elliptic Functions." By Colonel R. L. HIPPLEY.

FARADAY SOCIETY.

Ordinary Meeting, May 9, 1916.

Sir ROBERT HADFIELD, F.R.S., President, in the Chair.

MR. EMIL HATSCHEK read a paper entitled *"An Analysis of the Theory of Gels as Systems of Two Liquid Phases."*

The generally accepted theory of the constitution of gels is that they are systems of two liquid phases. No attempts have been made to determine whether this assumption accounts for various observed properties of gels. The present paper is a mathematical investigation directed to

determining whether the observed elastic properties of gels are compatible with their being composed of two liquid phases only. If this is the case it follows that their elasticity must be due exclusively to the interfacial tension between the phases, viz., the work done in stretching a cylinder of gel must be equal to the surface energy developed. It follows immediately that the function connecting stress and elongation must be the first differential of that connecting surface and elongation. To obtain the latter various structures, consisting of space-filling polyhedra, such as rhombohedra, rhombic dodecahedra, and cubes are examined and the increase in surface calculated for deformation in the direction of principal axes. The curves obtained by plotting surface as ordinates against elongation as abscissæ are similar in all cases and obviously represent the same function, although analytical treatment is only carried out for one case. Since the curves all show an inflection it follows that the stress reaches a maximum at the elongation at which the inflection occurs and then decreases—i.e., to stretch the gel beyond this point a smaller stress would be required than for a smaller elongation. This, as well as the shape of stress-elongation curves obtained experimentally, which differ very considerably from the theoretical curve, shows that the assumption of two liquid phases is inconsistent at any rate with the elastic behaviour of gels.

Prof. ALFRED W. PORTER, F.R.S., pointed out that Mr. Hatschek's criticism did not distinguish between an ordinary liquid and one as viscous, say, as cobbler's wax, which acted as a solid to forces applied rapidly. He thought, too, that in the case of two-liquid phases the straight-sided forms assumed would not persist in equilibrium; the continuous would shrink away from the disperse phase and form gaps unless the former were exceedingly viscous. Mr. Hatschek's argument was sound if polyhedra were formed.

Dr. C. H. DESCH thought the geometrical forms of the structure would be neither rhombohedron nor rhombic dodecahedron, but Kelvin's 14-sided polyhedron with curved faces.

Mr. HATSCHEK in his reply added that he conceived gels as of an ultimate crystalline structure, with the crystals thinned and filled with liquid.

In introducing two papers by Mr. F. C. THOMPSON, M. Met., B.Sc., the PRESIDENT expressed his appreciation of the encouragement the University of Sheffield gave to young metallurgists like Mr. Thompson in the prosecution of research, and he remarked on the value of the author's work. As an incentive to him he offered a prize of £50 to continue his researches and present the results to the Faraday Society.

The first of Mr. Thompson's papers dealt with *"The Properties of Solid Solutions of Metals and of Inter-metallic Compounds."*

By considering the space-lattice of a solid solution of two metals as resulting from the substitution of atoms of B for an equal number of A in the space-lattice of the latter it is possible to predict with some completeness the properties, hardness, specific volume, electrical resistance of the alloy.

The distortion of the space-lattice resulting from this substitution of other atoms of different atomic volume explains the generally marked resemblance of the properties of solid solutions of metals to those of a metal which has been mechanically deformed. An elementary mathematical treatment results in a parabolic curve, which corresponds with that practically observed for the relationship of hardness to concentration in a series of alloys, such as those of gold and silver, which form an uninterrupted series of solid solutions.

The influence of the atomic volume on the readiness with which solid solutions are formed and the properties of intermetallic compounds are also briefly considered.

Dr. C. H. DESCH suggested that an examination of solid solutions, such as that of gold and silver, by means

of Bragg's X-ray spectrometer might throw light on the structure of the space-lattice.

Mr. SYDNEY W. SMITH remarked that Roberts-Austen had long ago realised the importance of the gold-silver alloys as a means of attacking these problems.

Mr. THOMPSON then read his paper on "*The Annealing of Metals.*"

After briefly considering the structural changes induced in metals and simple alloys by such processes as rolling or wire-drawing, as a result of which the crystalline elements remain unchanged in hardness, the conditions governing such mechanical treatment of metals are examined.

The efficient commercial annealing of brasses, nickel silvers, cupronickel, &c., is shown to differ radically from that necessary in the case of steel, the lowering to a minimum of the elastic limit being essential to allow a maximum further reduction at the next rolling before a further annealing is required, and also to minimise the loss of energy wasted in the production of merely elastic deformation.

The course of annealing of hard-worked copper, brass, and nickel silver, taken as typical examples, is followed in some detail, and the influence of the temperature and duration of annealing and of impurities in the metal dwelt upon. A summary of Charpy's classical work on the annealing of hard-worked brass and of similar work by the author on the nickel silvers is given.

A paper sent in by Mr. ZAY JEFFRIES, of Cleveland, Ohio, on "*Grain Size Measurements in Metals, and Importance of such Information,*" was communicated by the PRESIDENT.

The author emphasises the value to the user of physical tests of metals. Now, physical and mechanical properties of metals vary greatly with changes in structure, and in the cases of pure metals and solid solutions the quantitative estimation of the structure can best be made by determining the grain size. Such measurements, however, only become important when correlated with the physical properties of the metal or alloy. The fact that these measurements do not break down the structure of the metal gives them a distinct advantage over mechanical tests in determining, for example, tensile strength or elastic limits, which are dependent on fineness of grain. The method is one of the best available for the determination of the relative quantities of crystalline and amorphous phases, and it is of special value in indicating the life of metals under vibration, in the estimation of the strength properties of alpha brass, in indicating hardness, and in all probability in throwing light on certain corrosion problems.

The following methods for measuring grain size are briefly described:—(1) The Planimeter Method; (2) the Heyn Method; (3) the Intercept Method; (4) the Method of Comparison with Known Samples; (5) the Author's Method. This method, for which great rapidity as well as accuracy is claimed, consists in counting the grains completely included and partly included in the circular portion of an image of the specimen of standard magnification, and by means of an empirical formula determining therefrom the equivalent number of whole grains in the standard area. The apparatus and manipulation required for the measurements are described in some detail and a few simple rules for sampling are laid down. In the interpretation of results care must be taken to distinguish between grain-size and cell-size. In cold-worked metals that have been annealed and sometimes in cast metals the grains will often be elongated, but in elongation due to cold-working measurements parallel and perpendicular to the direction of working show fairly constant ratios.

The PRESIDENT, in commenting on the paper, referred to the enormous tenacity attained by metals at extremely low temperatures, due probably to the closeness of grain. It was unfortunate that a limit was soon reached, for instance in hardened steel, below which the grain was too fine for Mr. Jeffries' method to be applied. He hoped

further research would overcome this difficulty; perhaps some method like Bragg's might be applied. He mentioned that whereas a 0.58 per cent carbon steel contained 5540 grains per square inch as forged and 4500 as forged and annealed the number rose to 330,000 when the steel was water-quenched and reheated.

Dr. C. H. DESCH agreed with the author that the Intercept method was not reliable.

Mr. F. C. THOMPSON, in the course of remarks on the relation of physical properties of iron and steel to grain size, said in these cases another factor had to be considered—namely, the fineness of the carbide in the grains as well as the size of the grains themselves. He preferred as a unit number of grains per unit length to number per unit surface. Shock tests gave a better measure of crystalline size than tensile tests.

Mr. S. W. SMITH suggested that the rate of corrosion might in some cases be used as a measure of grain size.

A paper by Dr. F. J. BRISLEE, on "*The Changes in Physical Properties of Aluminium with Mechanical Work (II. Specific Heats of Hard and Soft Aluminium),*" was read by Dr. R. SELIGMAN in the absence of the author.

A series of determinations of the specific heat of hard-worked aluminium and annealed aluminium was made. The metal was used in the form of rod and wire. It was found that the specific heat of the hard aluminium was higher than for annealed, and this confirmed the view that aluminium is converted into an amorphous form by excessive mechanical work. It was further found that the specific heat underwent a change when the hard-drawn bars and wire were heated to 100° C. A sample of wire was prepared by drawing with the maximum draught possible, whereby a high tensile strength was obtained, but the wire could not be bent without fracture. The worked metal had a tensile strength of 18.4 tons per square inch, and after heating to 100° C. for ten weeks the tensile strength was reduced to 13.2 tons per square inch, but whereas the original metal was brittle and could not be used the metal with the lower tensile strength was quite serviceable.

It is therefore necessary that the determinations of all the physical constants of metals shall be made upon metals in a perfectly definite state and one which can be reproduced. If this is not done the results are fortuitous and may differ widely from the true results.

Further investigation is being made to obtain aluminium wholly in the amorphous state.

Dr. R. SELIGMAN, while agreeing with the author's conclusions, was unable to see how he arrived at them from figures given in the paper. He criticised the author's use of different temperature-ranges for the various sets of experiments. Dr. Brislee's observation of the change of the specific heat of hard-worked aluminium under the influence of so low a temperature as 100° C. might possibly be of great technical importance. He did not agree that as a general rule aluminium after ten hours' heating at 500° C. was, although "dead soft," still largely amorphous in structure.

Dr. J. A. HARKER thought it a mistake only to take ordinary temperatures as the norm in studying the relation between composition and physical properties of metals and alloys. If the melting-point were taken as the starting-point in, say, a series of specific heat measurements, the matter of the previous thermal history of the specimen would not be a disturbing factor. There would be no great difficulty in devising a suitable calorimeter for such measurements.

Dr. R. SELIGMAN and Mr. PERCY WILLIAMS presented a "*Note on the Annealing of Aluminium.*"

The authors found that hard-worked aluminium which had been heated for ten hours at 125° C. was less readily soluble in nitric acid than the same metal before heating, but that if the heating were continued for eighty hours this comparative immunity from attack was lost.

They also found that metal which had been freshly

annealed at 440° C. was less readily attacked by nitric acid than the same metal which had been allowed to stand for ten days after annealing.

Dr. H. BORNs asked what precautions had been taken to prevent oxidation before making the solubility tests.

Dr. R. SELIGMAN said the samples were all immersed in caustic soda.

Mr. E. J. HARTUNG, B.Sc. (University of Melbourne), presented a paper entitled "*A Contribution to the Theory of Solution.*"

The author has tested the divergence in physical properties from those calculated by the simple mixture law shown by two completely miscible liquids which do not visibly react with each other. This divergence has been ascribed by Denison to solvate formation. The liquids used for the experiments were aniline, methyl alcohol, carbon tetrachloride, ethyl ether, and chloroform. Measurements were made of the density, heat capacity, and heat change in mixing of mixtures of selected pairs of these liquids.

The evidence adduced shows that in the cases examined no simple solvate theory will suffice to explain the experimental results, even though the liquids used with one exception are little associated. Also, a study of the deviation curves obtained from many other liquid-pairs by various authors leads to the conclusion that only in rare cases if at all will the conditions be simple enough to permit of an explanation of the deviations by single solvate formation. In the great majority of cases the molecular condition of a mixture of two liquids is much more complex, and it becomes very difficult to develop and apply any satisfactory quantitative theory.

Prof. ALFRED W. PORTER, F.R.S., said the author's experimental results were a valuable contribution to science and would be of great use to investigators, but he could not agree with his theory, based as it was on Denison's unsound equation. In the present state of our knowledge of mass-action we must be content to accumulate facts and deal empirically with them.

CHEMICAL SOCIETY.

PRESIDENTIAL ADDRESS, BY DR. ALEXANDER SCOTT,
F.R.S.*

(Concluded from p. 251).

DYES may be said to consist essentially of two distinct parts, to one of which the colour is due and to the other the power of fixing the colour on tissues. Many diseases are due to the life and the multiplication in the body of their host of multitudes of minute organisms termed protozoa, which in diseases such as sleeping sickness are known as "trypanosomes." Now Ehrlich found that the trypanosomes which he was investigating were always stained by certain dyes which chemical research had proved to contain a definite grouping of atoms in their molecule. The idea struck him that he might kill these minute creatures by obtaining a compound which contained this fixative group of atoms attached not to a colour-giving group but to one which would act as a poison to the protozoa. I need scarcely point out that a drug had to be discovered which whilst it killed the germ left the host unhurt. A series of such compounds was prepared in which the toxic element was arsenic. Each of these compounds had to be tested on the spirilla and on the higher living organisms of the host by Ehrlich and his assistants. It was not until 605 unsuccessful compounds had been prepared and laboriously tested that "No. 606," or "salvarsan," the chemical name of which is dihydroxy-diaminoarsenobenzene, was added to the list of successful drugs. Further research along similar lines has put

even more efficient curative agents into the hands of the physician.

Just as we have the two types of research broadly marked out, so have we the two types of men who enlarge our knowledge; the one who feels that he can best fulfil his life's purpose by devoting himself to discovering new substances and new laws with the simple purpose of increasing the store of natural knowledge, so that the man of the other type in due time may find uses for the substances, and by means of the laws discovered apply them to the solution of problems in the arts and sciences. For the first the sole reward is too often the pure joy of having succeeded in his aim, realising fully that the successful applications of his discoveries and the money prizes attached to such will never be his. The public—even the enlightened portion of it—is too prone to regard at the time such original work as entirely useless. It is impressed infinitely more by the discovery of artificial indigo, of salvarsan, and of antipyrin, and the manufacturer agrees in this. The latter usually wants his research chemist (if he be so enlightened as to secure the services of one) to indicate his presence in the works by a visible increase on the income side of the balance-sheet without any corresponding charge on the other side after, it may be, one or two or even three years' work, although he himself may, with a lifelong knowledge of the circumstances of his factory and its products, have been unable to effect this. In fact it is by no means seldom that a research chemist at a miserable salary is only engaged in the same way that a specialist is often called in when the patient is on his death bed—namely, as a last resort—whilst, had his assistance been invoked at an earlier stage in the malady it would have succeeded in achieving the desired effect. If the chemical manufacturer and those engaged in the allied industries are not only to hold their own but to save themselves from an extinction as certain as the death of every living organism there is only one remedy, and that is to call in the services of the man who has been trained in the methods of advancing knowledge and whose education has been based on a sound acquaintance of the fundamental facts and theories of modern science. To keep along the same dead level of a fair measure of success is an existence which can only satisfy a decadent race and can only last for a very limited time. Our race has again shown itself in this war to be as full of energy, bravery, and chivalry as of old, but it is only gradually learning how much the neglect of research and the want of appreciation of a scientific training and education has cost it. Even our law-givers and law-makers are having the importance of scientific knowledge and training forced upon them, and perhaps no branch of science has had its utility more strikingly demonstrated for the time being than our own. But it has required hundreds of thousands of tons of T.N.T., lyddite, and dynamite to shake the foundations of their ignorance. When those of our defenders at the Front who have escaped the scientifically organised atrocities of our enemies and the consequences of the scientific ignorance of our rulers return home again we may venture to hope for the dawn of a new era in chemistry, with perhaps brighter prospects of success than Boyle had two hundred years ago.

Our daily newspapers and our scientific journals have vied with one another in laying bare the various defects in our general and scientific education, organisation, and training so as to have left but little still unsaid.

It is evident that if the manufacturers are to employ properly trained chemists they must be provided with an adequate supply of men who not only know what is already known, and may be merely walking cyclopædias, but men who have been trained to attack problems. The famous mathematical school of Cambridge, which can point with pride to Newton, Stokes, Kelvin, Rayleigh, Thomson, and others, in its examinations makes a strong point of its "problem papers," in which neither the scientific nor even the cash value of the results are worth the paper on which the successful solutions are written. The training secured

* Delivered at the Ordinary Scientific Meeting, April 6, 1916.

thereby is such as to enable those who are successful to tackle with every chance of success any problem which may present itself in after life.

Throughout my life I have been associated with educational matters, and these have always interested me profoundly, although I may not have bombarded the *Times* or its readers with my theories on the subject.

The son of the head master of a large grammar school in the south of Scotland, I went first to the University of Edinburgh and thence to Cambridge, and after nine years' residence there I left to spend seven years in organising the science teaching in Durham School and Middlesbrough High School. Whilst there I had ample and unique opportunities of comparing the value of a classical with that of a scientific training from the purely educational viewpoint. After allowing fully for various social and other conditions at these two schools I have no hesitation in recording as the result of my experience that the science subjects possess a much higher educational and more stimulating value than the classical subjects.

There are, however, many points which our newspaper correspondents, who write so glibly on education, overlook when throwing blame on the various educational authorities for their many shortcomings.

In the first place, the head masters found it very hard indeed to obtain men who could really teach and keep order in a class of boys. To do this successfully meant that the science masters had been properly trained, and had such an intimate acquaintance with simple experimental methods that they did not require when showing, say, the union of hydrogen and oxygen in a eudiometer to stand back as if they were afraid of being shot, and ignorant as to whether the eudiometer, or the mercury, or perhaps both, were going to be distributed amongst the class. The teaching of chemistry was too often left to the junior mathematical master, who might also be asked to take the junior French class.

Again, in those schools which were fortunate enough to secure properly trained science masters they were expected to prove their value to the school not by sound, all-round fundamental teaching, but by devoting their spare time to the coaching up of the more promising of those boys who might be allowed to enter the despised "Modern Side" because they were not likely to gain a classical scholarship, but might possibly gain a scholarship in natural science. This in turn, because of the many absurdly advanced questions set in the entrance and other scholarship examinations at the various Oxford and Cambridge colleges, meant that candidates had to read and "get up" specialised branches of work of which at that stage they had better have been ignorant, devoting their energies instead to acquiring a sound knowledge of the principles and well-established experimental data underlying the various branches of science.

The evil does not end here, for if successful the newly elected scholar is usually too proud to attend the so-called elementary lectures of the professor, which would do him all the good in the world, but pursues his course of attending advanced and special courses, becoming a specialist long before he ought to do so, without having that broad base for his knowledge which is essential for true progress. His knowledge ought to be represented by the solidity of an Egyptian pyramid instead of resembling a truncated cone poised on its narrow end. Suitable as the latter type may be for the fellowship of a college, he is almost as unfitted as his fellow classic for active and useful life in an industrial centre and among industrial surroundings and problems.

The boy with brains at a public school who goes to Oxford or Cambridge, whose ambition is to lead the life of a student, devoting himself to intellectual pursuits in preference to going into any of the learned professions or into commerce of any kind, is taught to regard the fellowship of a college as the first and most natural aim of his ambition. To obtain this his schoolmasters point out that the chances of his gaining such a prize are much greater if

he studies classics, history, or mathematics rather than any branch of natural science, even although the colleges may state that the opportunities for science students are just as great as for those in any other subject. This is not so, for the simple reason that the electors to the fellowships are in almost all colleges mainly classical men, who even if they wish to be strictly fair, as they undoubtedly do, cannot estimate the real value of what they are unable to understand. Hence the selection when made is too often a picturesque failure from the scientific point of view. Again, in some well-known cases, with a powerful personality on the college council, all the fellowships which the college may devote to the encouragement of natural science are given exclusively to one branch of science, whilst other departments of science get none.

A concrete example will be more convincing and make my meaning more clear than any number of general assertions. I have therefore compiled the following analysis from the Natural Sciences Tripos lists, as given in the "Cambridge University Calendar for 1915–1916." These lists are now given for the last ten years only, but are sufficient to prove my point.

These ten lists contain the names of 122 candidates who have gained First Class Honours in Part II. of the Tripos, and are arranged under the following subjects:—

	First Class Honours.	Fellowships.
Physics	32	7
Chemistry	31	0
Mineralogy	1	0
Geology	11	2
Botany	13	1
Physiology	21	4
Zoology	11	3
Anatomy	2	0
Total	122	17

That is to say, that of the seventeen fellowships devoted to the encouragement of natural science *not one* has been given for proficiency in chemistry, whilst no fewer than seven have been allotted to physics with practically the same number of successful candidates. Are the chemists so inferior intellectually to all the other candidates as this would seem to indicate, or what is the explanation of this preposterous state of affairs?

Nor is it only the younger chemists who suffer in this way, for even university lecturers in chemistry may devote forty years to teaching and the encouragement of research amongst their pupils, and be themselves Fellows of the Royal Society, without being elected to a college fellowship.

Let us suppose the brilliant schoolboy selects chemistry as his subject and gains a scholarship, and takes all the honours possible in his college and university examinations, what is the prospect before him? He *may* be elected to a fellowship and be content to settle down to the pleasant life of the university and do his share in its teaching for what can only be regarded as a mere pittance. He may give up that and go to the Bar, where he may do fairly well now that scientific knowledge has some value, as disputes on patent and other subjects depending on chemistry are more frequent than they used to be. There is no prize held up before him such as, say, a bishopric, no chance of his becoming a Cabinet Minister or the holder of any high office in the State because he has proved himself to be a first-rate scientific man. At present any such proof seems to mark him out as unfit instead of being regarded as a special qualification.

What opening is put before him in chemical industry? What salaries or wages are offered to tempt anyone with brains above the average to direct his studies or research work with a view to preparing himself for any work relating to chemical manufactures? When the manufacturers learn to appreciate the value of men thoroughly trained in research work they will find the universities and technical

colleges amply fitted to train the men for them and more than willing to do everything in their power to assist them, but if they want a good article they must be prepared to pay for it.

The examinations for the Civil Service whether at home or abroad are all heavily weighted in favour of the classical and mathematical candidates. Everything which is calculated to test a man's ability to tackle an unknown problem, however simple in its nature, is carefully excluded by a cautiously worded syllabus, which details the range of the facts and the nature of the tests which may be applied.

Surely it is time to change this state of affairs!

NOTICES OF BOOKS.

On the Relation of Imports to Exports. By J. TAYLOR PEDDIE, F.S.S. Second Edition, Enlarged. London, New York, Bombay, Calcutta, Madras: Longmans, Green, and Co. 1916. Pp. xxiv. + 148. Price 5s. net.

In this book the author puts forward a plea for the establishment of the new science of National Economics upon a thoroughly scientific basis, and urges the employment of exact scientific methods in the working out of the new national and imperial policy, which is one of the tasks now immediately before our leaders. He believes that it is most essential that the general public should have the facts and arguments put before them, and he gives a simple and clear treatment of the subject, which appears most opportune at the present moment. To the second edition an essay has been added on National Economics or Empiricism, which may be regarded as summing up his previous arguments. He believes that there are four main objects which the nation should aim at achieving:—(i.). The establishment of a Ministry of Industry. (ii.). The adequate representation in the House of Commons of industry, finance, science, and commerce. (iii.). The establishment of industrial banks. (iv.). The stimulation and encouragement of the standardisation of our educational system. The author's arguments are stated clearly and in temperate language, and the book can be recommended as deserving thorough study, which it will well repay.

Manuring for Higher Crop Production. By E. J. RUSSELL, D.Sc. (Lond.). Cambridge: The University Press. 1916. Pp. 69. Price 3s. net.

THE need for increasing the produce of the land is being constantly reiterated, and both the general public and those specially interested are beginning to realise that a good many changes must be effected in the near future. The need now appears to be for definite instructions, based upon the actual conditions as regards labour, costs of materials, &c., now obtaining, for the unworkable suggestions of enthusiastic theorists, who have no real practical knowledge of the subject under discussion, do more harm than good. Such direct instruction and advice based upon present day conditions is to be found in this book, which, however, must not by any means be regarded as having only a temporary value. It explains the methods which should be adopted to effect improvements in the soil, and gives short accounts of the nature and properties of artificial manures and their storage and application. The results of experiments upon the manuring of arable and grass lands are discussed, and the conclusions to be drawn from them are made clear. The author has chosen his material well, and put forward his facts concisely and without bias. The book cannot fail to be very useful to farmers in helping them to find out how to improve their production, and to agricultural students, in showing them the actual conditions to be taken into account in present day farming.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 15, April 10, 1916.

This number contains no chemical matter.

No. 16, April 17, 1916.

Catalysis of Hydrogen Peroxide in a Heterogeneous Medium. General Considerations. Experiments with Mercury.—Georges Lemoine.—In heterogeneous systems the decomposition of hydrogen peroxide depends only on the surface of the catalyst, or at any rate upon a very thin layer. Thus oxygen is very rapidly evolved with a layer of silver only 0.0002 mm. thick, deposited on glass by the ordinary methods of silvering mirrors. The activity of the catalyst depends upon the state as well as on the size of the surface. When equal quantities of catalyst were placed in identical tubes and were surmounted with unequal heights of hydrogen peroxide it was found that the relation between the height of the liquid and the volume of gas liberated varies with the concentration of the hydrogen peroxide. The author has repeated Bredig's experiments on the action of mercury upon hydrogen peroxide, and has observed that a red oxide of mercury is temporarily formed. When yellow mercuric oxide and H_2O_2 were brought together they react energetically and much heat is evolved.

Biochemical Synthesis of a Galactoside of Saligenine, β -Salicylgalactoside.—Em. Bourquelot and A. Aubry.—When saligenine and glucose in solution in acetone are treated with emulsine β salicylglucoside is obtained. The agent of this synthesis is β -glucosidase, the ferment of emulsine which intervenes in the biochemical synthesis of β -alcohol glucosides. A β -galactosidase is also present, and when the glucose in the above mixture is replaced by galactose a β -salicylgalactoside is obtained. The investigation of its properties shows that it is undoubtedly a β -monogalactoside of saligenine. Neither it nor the β -salicylglucoside has been prepared by a chemical method.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Royal Institution, 5. (General Meeting).
Society of Chemical Industry, 8. "Action of Nitric Acid on Aluminium," by R. Seligman and P. Williams. "Bacterised Peat—I. The Problem in Relation to Plant Nutrition," by W. B. Bottomley.
- TUESDAY, 6th.—Royal Institution, 3. "Optical Research and Chemical Progress," by T. Martin Lowry.
Röntgen Society, 8.15. "Homogeneity of Visible Radiation," by J. W. Nicholson. Exhibition of X-ray and Electrotherapeutic Apparatus.
- WEDNESDAY, 7th.—Society of Public Analysts, 8. "Determination of the Reichert and Polenske Figures of Butter and Margarine, using Small Quantities of the Fat," by A. Douglas Heywood. "Potash and other Mineral Fertilisers and Constituents of Plants," by R. R. Tatlock and R. T. Thomson. "Estimation of Acetone in the presence of Ethyl Alcohol," by J. Rakshit.
- THURSDAY, 8th.—Royal Institution, 3. "Chamber Music and its Revival in England," by Sir Alexander Mackenzie.
- FRIDAY, 9th.—Royal Institution, 5.30. "Eyesight and the War," by Dr. Ernest Clarke.
- SATURDAY, 10th.—Royal Institution, 3. "Folk Lore in the Old Testament," by Prof. Sir James G. Fraser.
Biochemical Society. (In the Biochemical Laboratory, Cambridge).

THE CHEMICAL NEWS

VOL. CXIII., No. 2950.

THE ESTIMATION OF FERRO- AND FERRICYANIDES IN THE PRESENCE OF CYANIDES AND THIOCYANATES.

By FREDK. G. W. KAPMAN and ERNEST L. RANDALL.

FERRO- and ferricyanides may be accurately and rapidly estimated volumetrically by means of a standard solution of titanous chloride.

All soluble ferricyanides are quantitatively reduced by titanous chloride in aqueous or slightly acid solution without the necessity for an external indicator.

Ferricyanides are first oxidised to ferriocyanides, and then titrated with titanous chloride.

The end-point of the reaction is indicated, in all cases, by the abrupt formation of a golden-brown precipitate (or a golden-yellow solution when the solutions are very dilute). It has been found that the reaction proceeds in such a way that 1 grm.-atom of ferric iron is reduced to the ferrous state for every grm.-molecule of ferricyanide present.

Preparation and Standardisation of Titanous Chloride Solution.—The standard solution of titanous chloride is prepared and standardised according to the directions given in Sutton's "Volumetric Analysis" (10th Edition, p. 234), except that it has been found better to use a somewhat stronger solution than that recommended by Sutton.

The solution is made so that 1 cc. of it is equivalent to about 0.0035 grm. of ferric iron and is standardised by means of pure ferrous ammonium sulphate, or by means of pure potassium ferricyanide in the way described below.

Estimation of Ferricyanides alone.—A definite volume of the ferricyanide solution is diluted, if necessary, until it contains roughly about 0.1 grm. ferricyanide per 50 cc. of titration mixture. An excess of ammonium or alkali thiocyanate (1 to 2 grms.) is added (preferably in the solid form), and titanous chloride is run in. The green colour of the solution deepens, then gets paler, and finally changes abruptly to a golden-brown precipitate. It is advisable to shake well before the addition of the last few drops of titanous chloride; i.e., when the solution begins to lighten in colour.

Amount of ferricyanide present in the volume taken = molecular weight of ferricyanide $\times$ number of cc. of titanous chloride used $\div$ iron value per cc. of titanous chloride $\div$ atomic weight of iron.

Estimation of Ferriocyanide alone.—The solution to be titrated is rendered slightly acid with H_2SO_4 , and dilute potassium permanganate (roughly N/20 is best) is added until the solution is yellowish red in colour. An ample excess of solid alkali thiocyanate is added (which destroys the excess of permanganate), the solution is diluted if necessary, and titrated as above.

(NOTE.—Too great an excess of permanganate should be avoided).

Calculated—1 grm. potassium ferriocyanide per 250 cc.

Found—(1) 1.001 grm.; (2) 1.002 grm. per 250 cc.

Mixture of Ferro- and Ferricyanide.—To a known volume of solution excess of solid alkali thiocyanate is added, and the ferricyanide is estimated in the usual way. The amount of thiocyanate added should be about twenty times the weight of the ferriocyanide present.

The total ferricyanide is estimated by oxidising another portion of the solution with dilute permanganate, destroying the excess with thiocyanate, and titrating with titanous chloride in the usual way.

The ferriocyanide may be calculated by subtracting the ferricyanide from the total. The results are accurate with large amounts of ferriocyanide compared to ferricyanide if a good excess of thiocyanate is used.

	$K_4Fe(CN)_6 \cdot 3H_2O$.	$K_3Fe(CN)_6$.
Taken . . .	2.5 grms. and	0.4 grm. in 250 cc.
Found . . .	(1) 0.499 grm. "	0.079 grm. in 50 cc.
	(2) 0.499 grm. "	0.078 " "
Taken . . .	0.5 grm. "	0.5 grm. in 250 cc.
Found . . .	0.499 grm. "	0.501 grm. in 250 cc.

Mixture of Ferriocyanide and Thiocyanate.—The ferriocyanide cannot be oxidised with permanganate since a white precipitate is formed which obscures the end-point. Several methods of oxidation were tried, but only one was successful, viz., iodine. To a portion of the solution a fair excess of, roughly, N/10 iodine is added, and the solution is warmed on the water-bath for twenty to thirty minutes at 50–60° C. The excess of iodine is removed by thiosulphate, in the presence of starch, excess of solid thiocyanate is added, and the solution titrated as before with titanous chloride.

Calculated quantity of titanous chloride required 7.0 cc.

Actual quantity of titanous chloride required (1) 7.05 cc., (2) 7.05 cc.

Mixture of Ferriocyanide, Ferricyanide, Thiocyanate, and Cyanide.—250 cc. of solution contained:—

0.2 grm. $K_3Fe(CN)_6$, 1.0 grm. $K_4Fe(CN)_6$, about 3 grms. KCN, about 3 grms. KCNS.

The alkalinity due to the cyanide was removed by adding a few drops of dilute sulphuric acid, using phenolphthalein as an indicator. A fair excess of iodine was added, and the solution treated as described in the previous paragraph.

This gave the total ferriocyanide plus ferricyanide. The ferricyanide was estimated in a separate portion of the solution by removing the alkalinity as above, adding considerable excess of solid thiocyanate, and titrating with titanous chloride.

Volume of titanous chloride required for 50 cc. of solution:—

(a) Calculated—9.05 cc. Found—(1) 9, (2) 9.05 cc.

Estimation of Ferriocyanides in "Spent Oxide."—This estimation is preferably performed on the residue left after extracting 5 grms. of "spent oxide" with carbon disulphide for the estimation of sulphur. The residue is triturated in a mortar with a crystal of ferrous sulphate (about 0.3 grm.), and 5 cc. of a solution of 8N caustic soda. The solution is filtered on the pump, washed, and the filtrate made up to 250 cc. Fifty cc. are acidified, oxidised as previously described with permanganate or iodine, excess of sodium thiocyanate is added, and the solution diluted to about twice its volume, and titrated with the titanous chloride.

The results obtained were checked by using Anderson's modification of the Feld-Witzcek method (see *Journal of Gas Lighting*, Aug. 3, 1915), and were found to be about 2 per cent too low; e.g., a sample of ordinary "spent oxide," which had not been specially worked for prussian blue, gave:—

By Feld-Witzcek method 4.49 per cent prussian blue, $Fe_7(CN)_{18}$.

By titanous chloride method 4.40 per cent prussian blue, $Fe_7(CN)_{18}$.

Other samples showed a similar difference.

Points to be Observed.

All the estimations described above can be made very accurate by attention to the following simple precautions:

1. The best dilution of the solution actually titrated is from 1 to 2 grms. of alkali ferricyanide per litre.

2. Avoid more than a slight excess of permanganate

and only use about sufficient dilute acid to decompose the permanganate.

3. Always remove alkalinity when cyanides are present.
4. Always use plenty of thiocyanate immediately before titration; *i.e.*, after the oxidation has been performed.
5. Shake well when near the end-point.

The reactions are not affected by considerable quantities of soluble chlorides or sulphates, provided these do not contain metals which can form insoluble double ferrocyanides with the ferrocyanides present.

Iodine may be used in place of permanganate throughout, only its action on ferrocyanides is much less rapid and the warming on the water-bath is necessary.

BENZENE: ITS SOLIDIFYING- AND MELTING-POINT.

By ROBERT MELDRUM.

THE following authorities state the melting-point of benzene to be as follows:—Regnault, 4.45°C .; Roscoe and Schlorlemmer, 4.5°C .; Allen, Bloxham, Mansfield, Strecker, 5.5°C .; Goodchild, Bayley, 6°C .; Mitscherlich, 7°C .; Fownes, solidifying-point, 0°C .; melting-point, 3°C .; Remsen, solidifying-point, 0°C .; Krauch, solidifying-point, 5°C . These variations may be due to the degree of purity of the sample operated upon, or to the absence of well defined melting- and solidifying-points, or both. Benzene is no different from innumerable other organic compounds in having various values published as their melting- and solidifying-points, boiling-points, gravities, and vapour-densities. The author has undertaken this investigation with the view of ascertaining if benzene has a well defined solidifying- and melting-point and the thermal conditions under which solidification takes place. For this purpose the author purchased the purest benzene available and obtainable, as time was not available for the preparation of a chemical pure sample. The sample so purchased was stated to be chemical pure. The thermometer used was a 50°C . divided into tenths, the zero-point being checked by immersion of bulb vertically in melting ice. The actual zero found was $+0.1^{\circ}$, all the readings being corrected for this error. During the experiments the thermometer was not allowed to rise above 9°C .

The solidifying- and melting-points were made in tube $6'' \times \frac{3}{8}''$, which had been well cleaned and heated to expel moisture and heated in desiccator previous to charging with benzene. The thermometer was used as stirrer and was fixed previous to taking readings.

Purity of the Benzene.

The purity of the sample was determined by solidifying 250 cc. in room temperature of 3°C . for twenty-four hours and draining away the liquid portion, which amounted to about 20 cc. This yielded the following results:—

T $^{\circ}$ room $^{\circ}\text{C}$.	..	..	..	3.5	3.5	4.0	4.0	3.0
T $^{\circ}$ benzene $^{\circ}\text{C}$.	..	..	..	5	6	7	8	9
Solidifying-point $^{\circ}\text{C}$.	..	..	..	3.5	3.9	3.9	3.95	3.9
Rise $^{\circ}\text{C}$.	..	..	..	0.9	0.9	0.5	0.8	1.0

Average solidifying-point, 3.92°C .

Attempts were made to produce higher temperature solidifications by very slow cooling with negative results, as will be seen from the following:—

Minutes cooling	0	10	20	30	40	50	60	70	80
T $^{\circ}$ benzene	..	7	6	5	4.5	4.2	4.0	3.5	3.3

Rising to 3.95°C .

Several tests were made by placing the tube directly in contact with snow to obtain rapid cooling, and as soon as solidification commenced removing tube and noting rise. By this method a solidifying-point also of 3.9°C . was

obtained. The bulk sample of 250 cc. was melted and again allowed to crystallise at 3°C ., when another 10 cc. of non-crystallisable was obtained; this was repeated a third time, but no liquor drained away. Three determinations of solidifying-point of second fraction gave 3.9°C . Maintained at 1°C . for twelve hours, not all solid but some liquid in centre. These results point to the fact that this sample of chemical pure benzene is not pure. But the question of course must be left open as to whether chemical pure benzene on prolonged keeping undergoes changes which result in a low melting-point product.

Solidifying Phenomena of Drainage.

During the above experiments it was observed in every case that at the moment of solidification a shower of fine crystals were formed, about 10 per cent of the whole, which immediately were precipitated to the bottom, the rate of crystallisation then slowing down enormously. At the same time a thin layer of crystals attach themselves to sides of tube. Even ten minutes stirring at 3.9°C . does not increase much the bulk of the crystals. In another experiment the drainage was cooled down to 2.6°C . for fifteen minutes after solidification had commenced, and even then only about 50 per cent had crystallised. When the temperature was allowed to rise slowly to 4°C . no rise was observed. Here then is the fact that complete solidification does not take place in the presence of excess of crystals while supercooled, and that no secondary shower of crystals takes place. It was also found by supercooling the drainage to 2°C . for twenty minutes after solidification commenced the test was nearly all semi-fluid. Exposure for twelve hours to a room temperature of 10°C ., the drainage registering 1.5°C ., complete solidification does not result, there being present about 50 per cent crystals and 50 per cent liquid.

Melting-point of Drainage.

It was considered necessary to determine the ratio between melting- and solidifying-point. Twenty cc. were cooled down to -10°C . till all solid and hard and free from liquid. The tube was now removed into air-jacket at 9°C ., and allowed to half melt and stirred with thermometer. The temperature remained constant at 4.0°C . during fifteen minutes. This was repeated five times with the same result. The melting-point is therefore 4.0°C ., or nearly same as solidifying-point.

This method is one of the most accurate and reliable for determining melting-points, and is superior to all other methods when it can be used. The melting-point can be determined during a long time interval. By allowing the crystals to fall to the bottom and the temperature of liquid to rise 0.2° above the solidifying-point and then stirring up crystals till temperature ceases to fall, gives very definite readings.

The Benzene Crystals.

Twenty grms. of the crystals were removed and crushed, and pressed between filter-paper at temperature of 3°C . to remove last trace of uncrystallisable, and the solidifying-point determined after melting at 9°C .

T $^{\circ}$ room $^{\circ}\text{C}$.	..	..	..	2	3	3	4
T $^{\circ}$ benzene $^{\circ}\text{C}$.	..	..	..	6	7	8	9
Solidifying-point $^{\circ}\text{C}$.	..	..	..	5.6	5.6	5.6	5.6
Rise $^{\circ}\text{C}$.	..	..	..	0.1	1.2	0.9	1.0

Average solidifying-point, 5.60°C .

Average melting-point, 5.70°C .

What takes place during solidification is that at the supercooled temperature a shower of crystals immediately forms which precipitates to bottom, the temperature rising to solidifying-point. These crystals amount to about 10 per cent of the whole, then crystal formation slows down greatly. Twenty minutes after, solidification commences in air-jacket at 4°C ., and twenty minutes in ice temperature has only fallen to 5.1° , when about 50 per cent is still liquid.

Slow Rate of Crystallisation.

That this particular sample of benzene has a very slow rate of solidification will be seen from the following experiment. Tube $\frac{3}{4}$ " $\times$ 6" about quarter full cooled in air-jacket at 3° C., in room temperature of 3° C.

T° benzene.	Mins.	
4.2	0	Solidification commences.
5.6	1	Rise completed, about 10 per cent crystallised.
5.4	60	Nearly all liquid.
5.4	90	About 50 per cent still liquid.
5.4	90	Placed in melting snow.
5.3	120	About 50 per cent still liquid.

That is, in two hours the benzene has only fallen in temperature 0.3° C. It is this slow rate of crystallisation more than anything else which leads to false melting- and solidifying-points. The slow thermal external exchanges would point to the fact that the benzene molecule at the solidifying-point becomes more complex.

The Superfusion of Benzene.

Benzene may be maintained in the superfluid condition for prolonged periods, as may be seen from the following experiment:—200 cc. pure benzene in stoppered bottle at a temperature of 15° C. exposed to room temperature of 3° C. for forty-eight hours remains quite fluid and free from crystals, but on disturbing or shaking a shower of fine crystals form, precipitating to bottom, and amounting to about 10 per cent of whole, the temperature rising to 5.6° C. As to be expected it is very difficult to obtain superfluidity in open tubes.

Colloidal Benzene.

In the course of the above investigation the author has observed that benzene cooled in tubes of various bores and stoppered bottles under various thermal conditions usually assumes a fairly well defined crystalline form, but in other cases absence of crystalline structure was observed. A tube of 1 inch bore half full of benzene was allowed to solidify in a room temperature of 1° C., the thermometer in benzene indicating 2° C. after forty-eight hours. This was free from crystalline structure and as transparent as water, and no doubt in the colloid condition. When removed from tube it was found to be tough like camphor, and easily fractured under slight pressure. In another case, but more pronounced, a stoppered bottle containing the pure benzene experimented upon, after being in a temperature of 2° C. for over twelve hours, was found to be a solid transparent mass free from traces of irregular form. Four large irregular cracks extended right through the mass, being very prominent on sides of bottle. A very close examination of this sample shows it to be benzene in the colloidal form. In some instances the writer has observed that on shaking bottles of superfluid benzene the liquid for a moment is of very high viscosity, which disappears when crystals begin to form. Most likely this is a solution of solid colloid in liquid benzene. It would appear that these changes of state are closely related to the slow rate of crystallisation, and points in the direction that the benzene molecule at these temperatures becomes more complex than normal.

Boiling-point of Benzene Crystals.

The purified crystals as used in the above tests gave a constant boiling-point of 80.05° C. to 80.15° C. for 95 per cent distilled over, the remaining 5 per cent being all over at 80.8° C. The thermometer used was graduated 50° to 100° C., divided into tenths. No reliance is to be placed on boiling-point of last fraction, as the increase of 0.65° is most likely due to superheating of vapour. The fact remains that the boiling-point is constant under good conditions. This is 0.45° C. lower than the usually accepted boiling-point of 80.5° C. It seems to the author that the purity of a compound like benzene cannot be determined from the boiling-point alone, but must be

ascertained from the ratio of melting-point and boiling-point. This ratio is very uncertain. Regnault's benzene with melting-point 4.45° C. had a boiling-point of 80.36° C., but there is no doubt his melting-point is too low, which would affect the boiling-point. On the other hand, Mitscherlich, who prepared his benzene from benzoic acid, found melting-point 7° C., boiling-point 85.5° C. Mansfield found melting-point 5.5° C. and boiling-point 80° C., nearly the same as the author's figures. Adriezen prepared benzene from crude benzole and benzoic acid, and found respectively boiling-point 80.53 to 80.62° for the former and 80.60 to 80.67° for the latter. Some years ago the writer attempted to produce pure benzene from 90 per cent benzole by a lengthy fractional distillation and freezing, but the purest product obtainable had boiling-point 83° C.

Summary.

From the results of the above investigation and the various published constants relating to benzene it would seem that this compound above the melting-point exists in one or more modifications, the molecule becoming more complex, which is the main cause of variation in its constants. The apparent existence of solid colloidal benzene and solutions of same support this; also the slow rate of crystallisation. There also seems to be some evidence from the writer's observations, which are not yet completed, that the melted crystals on keeping yield fractions with lower melting-points than the crystals. Also the solidifying- and melting-point method is more accurate in determining the purity of pure benzene than the boiling-point.

A NOTE ON THE ANNEALING OF ALUMINIUM.*

By RICHARD SELIGMAN and PERCY WILLIAMS.

It has been shown by various workers that hard worked amorphous metals undergo changes at comparatively low temperatures. Thus Beilby (*Trans. Faraday Soc.*, 1915, x., 212) points out that a rapid release of strain occurs in hard worked metals at 100° C., whilst Lowry and Parker (*Journ. Chem. Soc.*, 1915, cvii., 1005), when studying the specific gravity of aluminium filings, observed a decrease in the gravity when the filings were heated to 100° C. Recently Brislee has observed changes in various physical properties of aluminium at 100° C. (private communication).

During the course of a long series of experiments upon the solubility of aluminium in nitric acid it has been noticed incidentally that by heating hard worked metal to 125° C. a definite change in the rate of dissolution is brought about. Hard worked aluminium is more readily soluble in nitric acid than the same metal when annealed. Thus, for instance, a sample of hard worked aluminium which lost 56 mgrms. per 100 sq. cm. per twenty-four hours when immersed in 1.42 nitric only lost 39 mgrms. when similarly exposed after being annealed at 500° C., a decrease of 30 per cent.

When the hard worked sheet was heated for ten hours at 125° C. it was found that the rate of dissolution had fallen from 56 to 33 mgrms. per 100 sq. cm. per twenty-four hours. This is equivalent to a decrease of 5.3 per cent. Strips heated at 100° C. instead of 125° C. gave similar results, although the reduction of the rate of dissolution was somewhat smaller—namely, about 3 per cent.

It was anticipated that if the heating were prolonged the decrease in the rate of dissolution might be augmented. This was not found to be the case, but, on the contrary, as the heating at 125° C. was prolonged the fall in the rate of dissolution diminished, until samples heated for eighty hours at 125° C. showed the same or even a slightly higher rate of dissolution than samples which had not been

* A Paper read before the Faraday Society, May 9, 1916.

heated at all. This reversal was not noted in the case of samples heated at $100^{\circ}\text{C}.$, but was observed in a large number of samples heated at $125^{\circ}\text{C}.$

The facts recited do not appear to tally completely with the observations of other workers. A release of strain as indicated by Beilby should be accompanied by a reduction in the rate of dissolution, but such a release of strain would not account for the subsequent increase. An allotropic change such as Cohen and others describe for many metals would fit in with the changes in the rate of dissolution observed but for the fact that the reversal took place at the temperature which had brought about the first change. Finally Brislee appears to differ from all others in that the change he observed went much further and seemed to indicate progressive crystallisation even at $100^{\circ}\text{C}.$

A further anomaly has been observed in dealing with metal annealed at higher temperatures. It has been noted on many occasions that aluminium which has been freshly annealed has a lower rate of dissolution in nitric acid than a sample of the same metal which has been allowed to stand for several days after annealing. Thus, for instance, a sample of metal which when freshly annealed at $440^{\circ}\text{C}.$ dissolved in nitric acid at the rate of 31 mgrms. per 100 sq. cm. per twenty-four hours dissolved at the rate of 36 mgrms. thirteen days after annealing. On re-annealing at $440^{\circ}\text{C}.$ the rate of dissolution fell again to 32 mgrms. per 100 sq. cm. per twenty-four hours.

Attention is drawn to these facts in the hope that it may be possible for some of those who are interested in these changes to investigate them more closely, as the present authors are not likely to have an opportunity of pursuing the matter further.

SOME NEW METHODS OF TESTING FOR MOLYBDENUM.

By JAMES MOIR, M.A., D.Sc.

It is well known that a fugitive deep blue coloration is obtained as the first stage in the reduction of molybdic acid by nascent hydrogen. Chapman and Law (see *Analyst*, 1907, p. 251) by using platinised zinc with a sulphuric acid solution of MoO_3 succeeded in obtaining this coloration in a comparatively stable form and by titration with permanganate showed that it corresponds to Mo_2O_5 (or possibly Mo_3O_8). On further reduction the solution passes through green and olive to chocolate brown, when the titration shows that the state of oxidation is Mo_2O_3 . This chocolate coloration is the one ordinarily obtained when zinc and fairly strong acid are employed, whereas tungsten under these circumstances always gives blue precipitates not colorations. From the intensity of the deep blue coloration the author expected that a specially sensitive test for molybdenum could be devised if conditions could be hit on under which any too extensive reduction to Mo_2O_3 could be prevented. For example, if the molybdic acid is present in a solution only faintly acid with mineral acid and this is treated with a few drops only of highly dilute stannous chloride a deep blue coloration of some stability is obtained; too much acid or too much SnCl_2 causes the test to fail, as the brown colour of full reduction then obtained is not sensitive. The use of acetic acid instead of mineral acid in this test is of no advantage, as in this case the addition of dilute SnCl_2 produces only a yellow turbidity turning brown and not at all sensitive.

Hydrazine, N_2H_4 , forms in the writer's experience the best reagent for developing the blue colour. A solution containing a trace of alkali molybdate when acidified with acetic acid and treated with a little hydrazine sulphate and boiled rapidly turns deep blue and retains this colour on boiling. Hydroquinone may be used in place of hydrazine with much the same result. An analogous but more re-

markable reaction is that obtained when a slightly acid solution of MoO_3 is treated with potassium iodide (in some excess) and boiled for some time; iodine is slowly liberated and the solution turns blue. The use of phenylhydrazine for reducing molybdenum has been described by Spiegel and Maas (*Ber.*, 1903, p. 513), but the reddish coloration obtained is different and seems to contain phenylhydrazine. Simple hydrazine is an improvement.

The best known sensitive test for molybdenum is that in which the acid solution is treated with sulphocyanide and a tiny piece of zinc added, when a crimson coloration is obtained in a few seconds. If iron is also present the solution becomes blood red on adding the sulphocyanide, but on adding the zinc this becomes colourless through reduction (to the ferrous condition) and after a few seconds becomes crimson if Mo is present. If the solution is strongly acid the coloration verges to red and is less sensitive, if nearly neutral the coloration resembles that of permanganate. It is probably due to $\text{Mo}(\text{SCN})_3$. Another modification of the test for Mo in presence of Fe is to add stannous chloride to the acid solution until the yellow colour just disappears and then add sulphocyanide.

Another well-known reaction for MoO_3 in the absence of iron consists in adding potassium ferrocyanide. Mineral acid must be present, and a russet-brown precipitate is obtained which still contains hexavalent molybdenum.

In the presence of acetic acid (not mineral acid) tannin (or gallic acid) gives a similar reaction, which has been known for some time. The writer has improved this by substituting pyrogallol or pyrocatechol for tannin. Either of these when added to a molybdic acid solution previously treated with sodium acetate gives a very sensitive orange coloration.

The facts contained in these papers were communicated to the South African Association of Analytical Chemists in May, 1915.—*Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, xvi., No. 8.

NOTES ON A NEW PROCESS OF BLEACHING.*

By S. F. PECKHAM.

SOME years ago a man brought to me some flax fibre and asked me to bleach it by a quick process without injury to the fibre. He said that a certain party that he named claimed to have done it. I said to him, "You will have nothing left but paper pulp," and after some talk he owned up that that was the case.

I knew that about thirty years ago one Charles Toppan had taken out a patent for a bleaching compound of which petroleum and the fixed oil of mustard were the essential ingredients. Great claims were set forth for this mixture, but nothing came of it, as there was too little fixed oil of mustard produced in the world to supply the demands of one large bleachery. At that time the only petroleum on the market was Pennsylvania petroleum, and it was a well-known fact that the crude petroleum and its distillates would dissolve in a solution of soap. A study of this process from all available sources led me to conclude that Toppan's compound, which was originally a lubricating compound, consisted of a fixed mustard-oil soap dissolved in petroleum, and that by varying the proportions his bleaching compound consisted of petroleum or its distillates dissolved in a solution of fixed mustard-oil soap.

A complete study of the chemistry of the fixed oil of mustard led me to conclude that any other pure vegetable-oil soap might act in a similar manner. The cheapest oil soap of that description on the market is what is known as cotton-oil soap stock. Having procured some of this I proceeded to make a solution of Pennsylvania petroleum distillate in a solution of the soap. This oil readily dis-

* Paper presented at the Eighth Annual Meeting of the American Institute of Chemical Engineers. From the *Journal of Industrial and Engineering Chemistry*.

solved and on boiling the flax in the solution it came out in a condition to be readily bleached in bleaching solution, but I concluded that the result was not wholly satisfactory, as the bleaching solution had to be so strong or the immersion had to be so long that the fibre was tendered.

I then concluded that I would try all the hydrocarbons on the market that came within range of practicability as to price and sufficiency of supply. I first made up a solution of a distillate of California petroleum, and on boiling and bleaching the flax it came out very much better in every respect. Reflecting on the fact that California petroleum consists of benzol and its derivatives while Pennsylvania petroleum consists of paraffins, the idea occurred to me that perhaps still better results could be obtained by using pure or nearly pure benzols.

I found that the different benzols dissolved in soap solution much more readily than the petroleum distillates and that the cleansing effect on the flax fibre was marvellous. Immersion in a very dilute bleaching solution produced a perfect dead-white bleach and left the fibre unimpaired in strength; in fact I had accomplished precisely what the gentleman had asked me to do.

This method can be successfully applied to all vegetable fibre, as linen is the most difficult to bleach of all of them without injury to the fibre.

I have never seen any mention made in chemical literature that benzol and its derivatives are soluble in a solution of soap nor did I ever hear any statement to that effect. No fixed formula can be designated, as soap is soluble in water in all proportions, and the stronger the solution of soap the more benzol the solution will dissolve. The formula used for 100 lbs. of flax was:—Water, 50 gallons; soap, 10 lbs.; benzol, 3 gallons.

This was used for a heavy woven linen damask, where for ordinary light cottons, such as "grey cloth," very much less material is necessary. Pure benzol need not be used; any of the light distillates of coal-tar, coke-oven tar, or blast-furnace tar, freed from impurities by washing and proper treatment, answers the purpose equally well.

My invention consists of a process of bleaching by substituting for the usual lime and soda boils a single boil in a solution of soap, preferably a pure vegetable oil soap, in which is dissolved a sufficient quantity of benzol (C_6H_6) or its homologues or derivatives as found in the light distillates of coal-tar and similar liquids and in light distillates of some varieties of petroleum, especially that of California, as distinguished from the light distillates of paraffin petroleum. The strength of the solution in both soap and benzol would depend upon the kind and character of the material to be bleached, light cotton fabrics requiring less than heavier cottons, and any cotton less than flax, jute, or hemp.

After thorough squeezing and washing to remove the soap solution the goods or fibre may be bleached in any known chemic. I prefer one of my own preparation, consisting of a solution of sodium hypochlorite, prepared by pouring together (cold) a solution of 58 per cent soda ash and a solution of calcium hypochlorite, stirring the mixture and allowing it to settle. Both solutions should be prepared cold, and after mixing the solutions they should be allowed to stand at least four days or until all the available chlorine in the calcium hypochlorite shall be found in combination with the sodium and in solution. No formula can be assigned for this mixture, as calcium hypochlorite varies indefinitely in strength. The quantities taken should be such that there will be a slight excess of the sodium carbonate. After a great many experiments upon this chemic I have found this method of preparation, which is very unlike any which is laid down in the books, to be the only one that will bring all the available chlorine in the calcium hypochlorite into solution as sodium hypochlorite. It is better to prepare this solution of a strength 3 to 5° Twaddell and dilute it to such a strength that an immersion of the goods from three to five hours will effect a bleach. After washing the bleached goods in water they are soured, washed, and calendered as usual.

By this method a complete bleach of either cotton or linen can be had in from one to two working days.

I have described a process of bleaching by which the goods or fibre are prepared for the chemic by boiling in a solution of soap in which has been dissolved a sufficient quantity of benzol or its homologues or its methylated derivatives, either separately or mixed together, as found in coal-tar naphthas and similar liquids, and the distillations from some petroleum as above set forth.

The soap which I have used is the cheapest that I know of on the market, as it is a by-product of the refining of cottonseed oil and is used in its crude state without further treatment.

The apparatus used is a Kier with a steam jacket, to which is attached an inverted condenser which returns the evaporated hydrocarbons to the Kier. The process was applied on a small scale and thoroughly tested out, with the most gratifying results. Of course the goods are singed and sheared, as is customary. Goods in small pieces were digested for various periods of time and the resulting goods subjected to a great variety of tests, excepting the effects of time upon finished goods. It was found that if the goods were thoroughly dried after thorough washing to free them from soap the effect of the chemic was very much more satisfactory than when they were introduced into the chemic damp, directly from the squeezers. This is not surprising when very dilute solutions of chemic are used, as the water remaining in the goods from the squeezers not only dilutes the chemic still further but filled the pores of the goods, thus getting in the way of the chemic and preventing it from doing its work.

An application was made for patent on the above process with the confident expectation that a valuable invention had been perfected, but the officials at the Patent Office in Washington quoted Toppin's and other patents against me, and I found that no amount of argument would convince them that there was the slightest difference between the substances designated "benzine" and "benzene"—in fact they declared they were identical. Comment is unnecessary in this place upon such a highly unscientific administration of the patent laws.

AZULENE, A BLUE HYDROCARBON.*

By ALFRED E. SHERNDAL.

SINCE the publication of the preliminary notice of the isolation of the remarkable new hydrocarbon which occurs in so many of the essential oils (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 167), the following further work has been carried out, and is described below.

1. The preparation of a picrate, and its analysis.
2. The preparation of artificial blue oils from various oils of the sesquiterpene type.
3. The isolation and identification, by means of the picrate, of azulene from the blue sections of the oils of cubebs, camphor, and from the artificial blue gurjun oil.
4. The complete reduction of azulene to a colourless dihydrosesquiterpene.

The picrate is readily formed by combining the alcoholic solutions of its constituents, and crystallises out almost immediately in the form of jet-black shiny needles, melting without decomposition at about 120°, and containing 1 molecule of picric acid to 1 molecule of azulene. This ready formation of a picrate is strong evidence that the hydrocarbon possesses an aromatic structure, since only this class of hydrocarbons has been found to yield additive compounds with picric acid, &c. (Bruni, *Chem. Ztg.*, 1906, xxx., 569; Küster, *Ber.*, 1894, xxvii., 1101). No true picrates of the hydroaromatic hydrocarbons have been prepared, the so-called picrates of pinene and

* *Journal of the American Chemical Society*, xxxvii., No. 6.

thymene (Lextreit, *Comptes Rendus*, 1886, cii., 555; Semmler, "Die Ätherischen Öle," II., 253), being in reality picric acid esters, from which the original hydrocarbons cannot be regenerated. They also differ from the picrates of the aromatic hydrocarbons in conditions of formation, stability, &c. The picrate of azulene, on the other hand, resembles the true additive compounds of picric acid with the aromatic hydrocarbons in ease of formation, decomposition by water or dilute alkalis, with regeneration of the original hydrocarbon, melting-point, &c. It provides an excellent means of establishing the identity of the blue substances isolated from various oils, and of effecting a final and complete purification of the blue hydrocarbon.

The method of preparation was as follows:—To a solution of 1.0 gm. picric acid in 20 cc. 95 per cent alcohol was added 1.0 gm. azulene dissolved in 5 cc. alcohol. In a few minutes the mixture set to a mass of crystals which dissolved again when warmed on the water-bath, and on cooling separated out in short shiny black needles. These were filtered off on the pump, and dried *in vacuo* over sulphuric acid. Yield, 0.73 gm.; m.p. 118°. The picrate dissolves readily in alcohol, acetone, and ether with a green colour; in benzene and ethyl acetate with a blue colour. The green colour of the solutions is probably due to partial decomposition in the moist solvents. For the same reason, if dilute alcohol is used in the preparation, a substance with a lower melting-point is obtained, more or less contaminated by oil. Carbon tetrachloride and benzene dissolve out the azulene and leave the picric acid undissolved. To determine the amount of picric acid in the compound, it was decomposed by warm water containing a measured amount of barium hydrate, made up to definite volume, filtered, and the excess of barium hydrate determined by titrating an aliquot portion of the filtrate with standard hydrochloric acid, using phenolphthalein as indicator.

0.445 gm. picrate, decomposed by warm water containing 17.6 cc. 0.1 N Ba(OH)₂, made up to 100 cc., filtered, and 50 cc. of the filtrate titrated with 0.1 N HCl. Required, 3.5 cc.

Found—54.3 per cent picric acid. Calculated for 1 molecule picric acid—53.5 per cent; for 2 molecules, 69.8 per cent; for half molecule, 36.6 per cent.

The picrate accordingly contains 1 molecule picric acid to 1 of the hydrocarbon.

The method of isolating azulene, which was described in the first paper, gives at least an approximation of the amount contained in the blue oil. As already shown, an intensely blue fraction which was examined yielded about 0.28 per cent azulene. Following the same procedure with a dark bluish green fraction of oil of cubebs, the amount of azulene which could be isolated amounted to only 0.03 per cent. This shows strikingly enough how oils containing only a trace of the substance might be intensely coloured and still show the characteristics of a homogeneous substance. To give an idea of the colour intensity of azulene, 0.064 gm. of the pure hydrocarbon was dissolved in a litre of benzene, and an ammoniacal solution of copper sulphate made up to match it in depth of colour. The latter solution contained 0.24 gm. CuSO₄ to the litre, and matched the azulene solution almost exactly both in depth and shade of the colour, showing only a slightly less purple nuance.

The azulene was extracted from the oil of cubebs as follows:—250 grms. of the oil were dissolved in 200 cc. of benzene, shaken out thoroughly in a separating funnel with 25 cc. of about 63 per cent H₂SO₄, allowed to settle during a half hour, and the acid solution then drawn off. This was then diluted with water and extracted with benzene. The same operation was repeated three times, and the final extraction of the diluted acid made with ether. On evaporation of the ether a residue of 0.073 gm. was left; i.e., 0.03 per cent of the cubebs oil taken. This residue was mixed with a solution of 0.07 gm. picric

acid in 2 cc. absolute alcohol. The black crystalline mass which soon separated was re-crystallised from a little alcohol, yielding then the characteristic black shiny needles of azulene picrate, m.p. 122°.

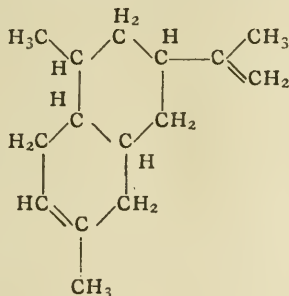
The production of blue oils from products which do not originally show any blue colour has already been referred to. Wallach (*Ann.*, 1894, cclxxix., 379) found that the hydrocarbon obtained by dehydrating guaïol with zinc chloride or phosphorus pentoxide showed a strong blue colour, and ascribed the colour to the presence of a small amount of some substance containing oxygen. Gadamer (*Arch. Pharm.*, 1903, ccxli., 33), in a similar manner, obtained a blue product by dehydrating atracytol, and noted also that guaïene, by the absorption of oxygen, took on a blue colour. α -Gurjunene, when heated under pressure with air of oxygen, yields a blue oil (*Ber.*, 1914, xlvii., 2252). All these colorations are undoubtedly due to the presence of small amounts of azulene, formed from the hydrocarbons by an oxidative process. Another reaction which produces azulene was suggested in the previous paper, namely, the action of sulphuric acid in acetic anhydride. By means of this reaction blue oils were prepared from the oils of amyris, guaïac-wood, and gurjun, and from the latter azulene was isolated and identified by means of the picrate. The sesquiterpene fraction of oil of eucalyptus also gave a greenish blue oil, while from oil of cedar-wood and caryophyllene of clove oil the distillates showed no trace of blue or green colour. The method of procedure was as follows:—

Ten cc. of gurjun oil were mixed with an equal volume of acetic anhydride and 2 cc. of strong sulphuric acid was added gradually, keeping the flask cool by ice-water. A violent reaction took place; the mixture took on an intense purple colour which changed to a dark blue, and sulphur dioxide was given off. After standing for some time steam was passed through the acid mixture, and a distillate of 4 cc. of a dark blue oil was thus obtained. By extracting the azulene from this oil in the usual way, i.e., by dissolving in benzene and extracting with 63 per cent sulphuric acid, a yield of about 0.04 per cent of the gurjun oil taken was obtained. The product gave a picrate which crystallised in coarse black needles with blunt ends, melting at 122°. The blue oils from guaïac, amyris, and heavy eucalyptus sesquiterpene were made in the same way.

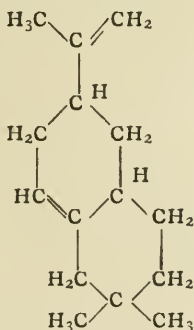
This is far from being a smooth reaction, which is not surprising considering the reagents used, but it shows, as do the other methods of producing blue oils, the nature of the reaction which results in the formation of azulene, namely, a splitting off of hydrogen by oxidative action, which results in the formation of new double bonds. In the terpene series we have the same reaction; that is, the oxidative removal of two hydrogen atoms from the compound C₁₀H₁₆, resulting in the formation of cymol, C₁₀H₁₄. This also is not a quantitative reaction, the yield of cymol being, as a rule, very low. But by such means the terpenes are converted into an aromatic molecule, which is structurally closely related to them. Now, all indications point to the conclusion that azulene also is an aromatic hydrocarbon. Its empirical formula, isomeric with the naphthalene homologue, C₁₀H₈.C₅H₁₀, its picrate, its high specific gravity, its behaviour towards sulphuric acid, are all evidence of aromatic structure. Once this is clear the striking analogy between the conversion of the terpenes, C₁₀H₁₆, on the one hand, to the benzene homologue cymol, and on the other and the conversion of the sesquiterpene, C₁₅H₂₄, to the aromatic molecule, C₁₅H₁₈, isomeric with a naphthalene homologue, becomes immediately apparent. The similarity of the reactions by which these conversions are affected adds still more to the analogy. Compare, for instance, the formation of cymol from camphor, with the production of the blue oil from guaïol, both by the action of P₂O₅; the formation of cymol from turpentine by heating under pressure with CO₂, with the formation of a blue oil by heating gurjunene under pressure with air or oxygen; the production of

cymol from various terpenes by the action of sulphuric acid, with the formation of azulene by the action of sulphuric acid and acetic anhydride on various sesquiterpenes. The assumption is certainly not far-fetched that an analogous oxidative process takes place in all these cases, which although not smooth yet from both classes of hydro-aromatic compounds tends to produce aromatic molecules of which the cyclic terpenes and sesquiterpenes respectively can be said to be hydro-derivatives. That the nucleus of the azulene molecule is not very different from that of the sesquiterpene from which it is produced is indicated by the experiment described below, in which its reduction to a colourless dihydro-sesquiterpene is effected.

If we could write formulæ to illustrate the structure of the various types of sesquiterpenes it would doubtless help to give an insight into the structure of azulene. The proposed formulæ for the sesquiterpenes are, however, based upon such meagre experimental evidence that they cannot be accepted as in the slightest degree conclusive. Some experimental evidence of their close relation to the terpenes and isoprene was given by Semmler (*Ber.*, 1914, xlvii., 2252), who succeeded in identifying terpinene in the degradation products formed by heating the gurjunene sesquiterpenes under pressure. In general, they are assumed to be hydro-naphthalene derivatives. Semmler (*Ber.*, 1903, xxxvi., 1038), in reviewing the possible condensations of three isoprene molecules, brings into consideration, on the basis of unpublished experimental data, the formula—



as the type of most of the sesquiterpenes, and states that this type can, under certain conditions, be readily converted into a naphthalene derivative. To another smaller class of sesquiterpenes he ascribes the type formula—



from which no naphthalene derivatives have as yet been obtained. It is evident that in these main types, pinene, camphene, or tanacetone rings can take the place of ethylene bonds. The sesquiterpenes also probably include open-chain and monocyclic compounds with a corresponding number of double bonds. The number of ethylene bonds, and consequently the ring structure, mono, bi-, or tricyclic, is determined by the molecular refraction, and in recent times the elegant method of reduction by hydrogen in the presence of finely-divided platinum or palladium, has provided an additional means

for determining the state of unsaturation, the monocyclic sesquiterpenes being thereby reduced to the saturated molecule C₁₅H₃₀, the bicyclic to C₁₅H₂₈, the tricyclic to C₁₅H₂₆. By this method it was demonstrated that azulene is tricyclic; that is, it contains four double bonds. It was reduced quantitatively to the saturated molecule C₁₅H₂₆, which then showed the characteristics of a tricyclic dihydro-sesquiterpene. The reduction was carried out as follows.—

Fifty cc. of 50 per cent alcohol and 0.2 grm. of colloidal palladium were placed in a shaking flask connected with a gas burette, the whole apparatus filled with hydrogen at ordinary pressure, and shaken by a mechanical arrangement till no more hydrogen was absorbed. With a current of hydrogen running through the flask, 2.552 grms. of azulene were introduced, the apparatus closed, and the shaking continued until the absorption of hydrogen ceased. The reduction required about twelve hours' shaking, the rate of absorption being uniform throughout and stopping suddenly. At 0°, 760 mm. about 1200° cc. hydrogen were absorbed. Calculated for H₈, 1146 cc. When the reduction was complete, as shown by the sudden break in the absorption of hydrogen, the mixture was distilled in a current of steam, and the oil collected in a narrow graduated tube. In this way were obtained about 2.5 cc. of oil with only a very faint green tint and the following constants:—

Sp. gr. at 25°, 0.8935; n_{D20} 1.490; O. R. $\pm$ 0.

The oil was insoluble in 63 per cent sulphuric acid, gave an intense coloration with acetic anhydride containing a trace of sulphuric acid, and also with bromine in acetic acid solution.

Comparing these constants with those of other tricyclic dihydro-sesquiterpenes it will be seen that the sp. gr. is considerably lower, indicating a differing structure. The colour reaction also shows that we have to do with a peculiar structure.

(To be continued).

THE PRODUCTION OF SULPHURIC ACID AND A PROPOSED NEW METHOD OF MANUFACTURE.*

By WILLIAM H. WAGGAMAN,
Scientist in Fertiliser Investigations.

Introduction.

THE importance of sulphuric acid in science, arts, and manufacture has been increasing steadily for many years. Although scarcely any industry exists which does not employ this acid either directly or indirectly in the manufacture of its product (W. C. Phalen, "Mineral Resources," 1913) the bulk of the sulphuric acid produced, both in this country and abroad, is used in the manufacture of fertiliser materials.

Since Liebig first proposed the treatment of bones or phosphate rock with sulphuric acid in order to render the phosphoric acid present water soluble, superphosphate has been the basis of the fertiliser industry and the economic production of sulphuric acid has been the aim of numerous investigators and chemical engineers. The production of sulphuric acid of various strengths in the United States for the past three years, according to the figures of the United States Geological Survey, is given in Table I.

Because of the difficulty in shipping such a commodity all of the sulphuric acid produced is consumed in this country. Some of the products manufactured therefrom are shipped abroad, but the quantity of acid entering into them is but a small percentage of the total production.

In 1913 the United States consumed 1,931,468 short tons of phosphate rock. Since practically all of this was

* Bulletin 283, U. S. Department of Agriculture.

made into acid phosphate at least 2,000,000 tons or over 56 per cent of the total sulphuric acid produced was thus consumed. A large tonnage of acid is also consumed annually in the manufacture of ammonium sulphate, a by-product of the coking and gas industries, and also in the production of what are known to the fertiliser trade as "base goods," consisting of acidulated hair, wool, tannage, or other nitrogenous refuse of the packing industry.

TABLE I.—*Production of Sulphuric Acid in the United States for the Years 1911, 1912, 1913, by grades.*

Year and grades.	Quantity. Tons.	Value. Dols.	Price per ton. Dols.
1911:—			
50° Baumé	1,026,896	5,447,958	5.31
60° Baumé	421,165	2,624,042	6.23
66° Baumé	751,541	9,176,297	12.21
Other grades	10,728	121,575	11.33
Total and average	2,210,330	17,369,872	7.86
Total reduced to 50° Baumé .. (a)	2,688,456 (a)	17,313,822	6.44
1912:—			
50° Baumé	1,047,483	5,378,411	5.13
60° Baumé	451,172	2,727,764	6.05
66° Baumé	774,772	9,360,630	12.08
Other grades	66,166	871,214	13.17
Total and average	2,339,593	18,338,019	7.84
Total reduced to 50° Baumé .. (b)	2,876,000 (b)	17,572,837	6.11
1913:—			
50° Baumé	1,643,318	9,212,917	5.61
60° Baumé	509,929	3,202,528	6.28
66° Baumé	797,104	9,282,422	11.65
Other grades	63,158	986,659	15.62
Total and average	3,013,509	22,684,526	7.53
Total reduced to 50° Baumé .. (c)	3,538,980 (c)	22,366,482	6.32
(a) Exclusive of acids of strength greater than 66° Baumé.			
(b) Exclusive of electrolyte and acids of strength greater than 66° Baumé.			
(c) Exclusive of 22,947 short tons of fuming acid, not convertible, valued at 318,044 dols.			

Methods of Manufacture.

There are two general methods employed in the manufacture of sulphuric acid—namely, the "contact process" and the "lead-chamber method." It is not within the scope of this paper to discuss in detail the numerous modifications of these two methods, but classified lists of the patents on the subject, together with short abstracts thereof, are given at the end of this paper.

The Contact Process.—Briefly the contact process consists in passing a purified mixture of air and sulphur dioxide, derived either from sulphur or burning pyrites, over some catalytic agent heated to dull redness, thereby effecting the further oxidation of the sulphur dioxide. The resulting sulphur trioxide is then usually absorbed in sulphuric acid, producing a very concentrated product.

Theoretically this should prove the simplest, cheapest, and most efficient method of making sulphuric acid, but in actual practice there are several details encountered both in the construction and running of a plant which unless given careful consideration will seriously affect the yield of acid and the cost of production.

Many different catalytic agents have been tried (notably platinum, palladium, iridium, the oxides or sulphates of iron, copper, chromium manganese, and silver, as well as the oxides of some of the rarer elements) in effecting the oxidation of sulphur dioxide, but no matter what catalyst is used its efficiency is seriously impaired and often de-

stroyed unless very elaborate systems are employed for purifying the gases before admitting them into the oxidation chamber. For instance, finely divided platinum (platinum black) has proved the most efficient catalyst so far discovered, but the catalytic power of this body in bringing about the union of sulphur dioxide and air is seriously affected by the smallest traces of arsenic in the gaseous mixture. When pyrites are used as a source of sulphur dioxide the arsenic which this mineral nearly always contains passes over with the furnace gases, and it is only by repeated washing and filtering that the last traces of this element can be removed.

Contrary to general opinion, therefore, a contact plant is both elaborate and costly, and strict supervision by a competent chemical engineer is necessary to ensure the best results.

The contact process has distinct advantages over the lead-chamber method where a pure concentrated acid is required, but in the manufacture of ordinary sulphuric acid (50 to 60° B.) for the fertiliser industry or for other purposes where the purity of the product is not essential, the latter method still holds first place (at least in this country) for efficiency and low cost of production.

The Lead-Chamber Process.—The lead-chamber process with its various modifications has been fully treated by Lunge ("Treatise on the Manufacture of Sulphuric Acid and Alkali," i.). This author, as well as numerous other investigators, notably Weber, Winkler, Rascheg, Meyer, Pratt, Gilchrist, Falding, and Wedge, has described details of construction, methods of accelerating the chamber reactions, and proposed and discussed schemes for increasing the efficiency and lowering the cost of acid systems. It is thought, however, that a brief general description of the chamber process will help toward a better understanding of the modification of the process proposed in this paper.

In this country nearly all of the sulphuric acid is made from pyrites. The lump ore is imported chiefly from Spain, while the "fines" are a domestic product mined in Virginia, Georgia, Tennessee, and California. If the lump ore is used it is burned in brick furnaces having grates composed of single square bars, which can be turned on their longitudinal axes to let the cinders down into the ashpits. Such furnaces hold from three to five tons each and are arranged in batteries of twenty to twenty-five for each set of lead chambers. The daily charge for each furnace when the system is in operation is from 750 to 1000 lbs. of pyrites. The burners for the pyrites "fines" consist of cylindrical furnaces having a series of shelves so arranged that the burning material can be mechanically raked from shelf to shelf until the fully burned cinder is discharged at the bottom of the furnace. The rakes are attached to a central air or water cooled shaft. In one type of furnace the shaft revolves, in another the shaft is rigid while the furnace itself revolves.

The gases from the pyrites burners are forced into a dust chamber fitted with baffle plates, where the oxides of iron, arsenic, lead, zinc, &c., are in a large measure removed. From the dust chamber the gases enter the Glover Tower, which consists of a lead tower (usually from twenty to thirty feet high and six to eight feet across) lined with acid-resisting brick and partly filled with quartz or other acid-proof material, so arranged that the dilute nitrous vitriol which is distributed from an apparatus at the top of the tower will trickle down through the interstices. The heat of the burner gases which enter the Glover Tower at a temperature of from 300 to 400° C. drives off water and the oxides of nitrogen from the nitrous vitriol, restoring them to the system. The uses of the Glover Tower therefore are threefold: first, to cool the furnace gases before allowing them to enter the lead chambers; second, to restore water and the oxides of nitrogen to the system; and third, to produce an acid more concentrated than that formed in the lead chambers.

From the Glover Tower the gases enter the first of the lead chambers, where most of the sulphuric acid is made. The lead chambers usually consist of large square or

oblong boxes made of sheet lead (weighing from six to eight lbs. per square foot) and having a capacity of from 25,000 to 75,000 cubic feet. (In the Meyer Tangent system the lead chambers are cylindrical in form, while in the Falding system their height is several times their length and width). Water in the form of fine spray or steam is introduced into the chambers at various points. This decomposes the nitrosulphuric acid formed into sulphuric acid and returns the oxides of nitrogen to the system, to be again acted upon by the furnace gases. The number and size of the chambers used vary from two to ten or more, depending on the number and size of the pyrites burners. Where the quantity of sulphur burned daily is large the acid plant is often divided into separate units, each battery of burners furnishing gases to its own set of lead chambers. The gases pass from the first to the second chamber and so on through the system, sulphuric acid being formed till the sulphur dioxide is practically exhausted.

The residual gases, consisting of nitrogen, oxides of nitrogen, some oxygen, and a small percentage of sulphur dioxide, then enter the lower part of the Gay-Lussac or recovery tower, which is similar in construction to the Glover Tower, except that it is usually taller and wider (from forty to fifty feet high and eight to fifteen feet across) and filled with coke instead of quartz. Strong sulphuric acid (1.5 to 1.7 specific gravity) trickles down the tower, absorbing the oxides of nitrogen from the residual gases, which ascend through the coke column and are finally discharged through a stack. The nitrous vitriol formed is then pumped to the Glover Tower, diluted with water, and distributed as previously described.

Measurement of a Plant's Efficiency.

The efficiency of a lead-chamber plant is measured, first, by the amount of chamber space required for each pound of sulphur burned in twenty-four hours and the amount of acid (50 or 60° B.) made therefrom, and, second, by the amount of nitre consumed or lost in the production of this acid.

Practically all sulphuric acid authorities agree that provided the gases are present in the proper proportions the two most important conditions necessary for efficient production are a thorough mixing of the gases and the control of their temperature.

The importance of the first of these conditions is self-evident, since in order to bring about complete chemical reaction the reacting substances must be in intimate contact with one another. The second condition is important because too low a temperature lessens the chemical activity of the gases, while a temperature above 100° C. prevents the condensation of water, which it is claimed is necessary to bring about the decomposition of nitrosulphuric acid, an intermediate compound formed from the oxides of nitrogen in the system.

Numerous schemes to control these conditions have been devised, some of which have features of considerable interest and practical importance. While it is impracticable in a paper of this length to discuss in detail all of these processes, several that have been tried, apparently with some success, are described below.

Methods for Accelerating the Chamber Reactions.

Walter and Boeing (German patent No. 71908) advocate the use of several hollow acid-proof partitions built across the chambers and so arranged that the gases enter the compartments through large holes near the bottom and are discharged from holes near the top. Numerous other small holes allow the admission and exit of the gases, thereby causing them to mix intimately without seriously interfering with the draught.

Because of the doubtful stability of these inner walls and the serious damage caused on their collapse this method is no longer used.

Gossage (Lunge, "Treatise on Manufacture of Sulphuric Acid," Part I., i., 475) as well as several other investi-

gators proposed filling the chambers with coke, so that the gases would be obliged to work their way through the interstices and thereby become thoroughly mixed. This scheme, however, has been abandoned because of the impurities introduced into the acid by the coke and the tendency of the coke columns to press against the lead walls, causing them to bulge and even break. The lack of any cooling device in this process also caused excessively high temperatures in the chambers.

Verstratt's (*Bull. Soc. Encour. Ind. Nat.*, 1865, 531) plan is similar to the above, except that stacks of bottomless stoneware jars filled with coke are used. The oxides of nitrogen are supplied to the system by allowing nitric acid to trickle down one of the stacks.

In Pratt's process (U.S. patents, Nos. 546, 596, 652, 687), which is much used in the Southern States, the gases are drawn through the first chamber by means of a fan, then through a tower packed with quartz, down which flows dilute sulphuric acid, and finally they are reinjected into the front of the first chamber by means of the same fan. This circulatory system seems quite efficient, and a number of plants where the process is employed are operating on less than nine cubic feet of chamber space per lb. of sulphur burned in twenty-four hours.

Meyer's tangential chambers are designed both to mix and to cool the reacting gases at the same time (English patent No. 18376; *Zeit. für Ang. Chem.*, 1900, 742).

The chambers are cylindrical in form, the first having water-cooled lead pipes suspended around the circumference. The gases are admitted at a tangent near the upper part of the chamber walls and are discharged from outlets in the centres of the chambers' bottoms. The gases are thus given a spiral motion, which tends to mix them thoroughly while the water-cooled lead pipes reduce their temperature.

There are three installations of this type of plant in the United States. One at least is reported to have given great satisfaction.

Hartmann (*Chem. Zeit.*, 1897, 877) obtained an increased yield of acid in the lead-chamber process by placing vertical air-cooled lead pipes in the chambers. The chamber bottom is turned up around the lower ends of these pipes, forming hydraulic seals, and thus obviating the necessity of joints in the bottom of the chamber.

Blau (German patent No. 95083) proposed to cool the gases in the first chamber by injecting a spray of cold sulphuric acid, and in order to obtain the optimum yield of acid from the gases in the subsequent chamber their temperature is raised by injecting sprays of warm sulphuric acid.

Falding's process (U.S. patent No. 932771, 1909) has for its object the segregating of the active gases in a system. To accomplish this he employs a chamber the height of which is approximately one and one-half times greater than its horizontal dimensions. The burned gases, after passing through the Glover Tower in the usual way, are introduced either near the top or lower down on the chamber's side. Since the fresh gases are hot, not only because they have recently issued from the pyrites burners but because of the reactions taking place between some of the constituents, they collect in the upper part of the chamber in a relatively active layer.

As the reactions subside the spent gases gradually cool and settle to the bottom of the chamber, where they are withdrawn. Falding claims that by using the high chamber a zone of great chemical activity is always maintained in the upper part of the chamber, and that the spent or inactive gases, which in ordinary chamber systems act as diluents, are continually being removed from the active zone. It is also claimed that much less chamber space is required to complete the reactions by this process, so that even where large volumes of gases are handled each chamber is a unit in itself, being connected directly with the Glover Tower instead of as in series, as in ordinary chamber systems.

A number of plants in this country are equipped with

chambers of this type, and it is reported that the process is commercially successful.

The main objections to the Falding system in the opinion of the writer are, first, that no provision is made for obtaining an intimate mixture of the gases other than the preliminary mixing brought about in the Glover Tower, and second, that no adequate means is provided for the condensation of the acid mist formed by the reactions.

The most widely used method of mixing and cooling the reacting gases is by means of intermediate towers containing plates, tubes, or baffles of some acid-resisting material, cooled either by water, air, or dilute sulphuric acid. A number of different types of towers have been designed, but mention is here made of only a few of the better-known designs.

Lunge's plate tower ("Treatise on Sulphuric Acid," Part I., i., 478) consists of a shell of lead either cylindrical or angular in form and filled with a series of perforated plates laid horizontally. Each layer of plates is supported at some distance above the other by bearers in such a way that every plate is independent of the others. The plates are so constructed and placed that the holes in those of one layer do not come directly above the holes in the next layer below.

Dilute sulphuric acid is allowed to trickle down the tower, splashing from one layer of plates to another and meeting the hot-chamber gases as they wind upward through the tower. The film of dilute acid over the plates presents an immense cooling surface to the gases and at the same time furnishes the water necessary for the decomposition of the nitrosulphuric acid. The formation of this latter compound is, according to Lunge, a necessary link in the chamber process.

Gilchrist's pipe-column system (*Journ. Soc. Chem. Ind.*, 1899, xviii., 459) consists of lead towers (three or four feet across and fifteen feet high), having corrugated lead tubes open at both ends, running through them horizontally, like a steam boiler. The sides of the towers are boxed in with boards, so as to form an air shaft, which terminates in a flue at the top.

The chamber gases together with water vapour enter the pipe columns at the sides near the bottom and work their way upward through the towers. Contact with the air-cooled corrugated tubes condenses the sulphuric acid, which then drips in showers from one series of pipes to another and frees the oxides of nitrogen, restoring them to the system. The gases issue from the top of the towers and enter the next chamber, from which they are drawn into another series of pipe columns, and so on through the system till their oxidation is practically complete.

While some of the methods just described are designed to cut down the amount of chamber space required, none of them, with the exception of Falding's process, reduces the initial cost of erecting an acid plant, for while less lead may be employed in constructing the chambers the expense of the cooling and mixing towers more than offsets the saving in chamber material.

Another objection to most of the accelerating devices discussed above is that in order to mix the gases thoroughly they must be drawn or forced through small openings, or made to pursue a meandering course by means of baffles or some acid-proof packing material in the towers. Under such conditions dust or impurities may clog the apparatus, choking off the draught and making it necessary to clean out the tower or chamber before operations can be resumed. Moreover, the collapse or disarrangement of the packing material within the tower may cause even more serious trouble.

Nearly all modifications of the chamber process complicate somewhat the running of an acid plant, and should therefore be constantly under the supervision of a competent chemical engineer.

In the new modification of the chamber method described in this publication a complete mixture of the gases and the control of their temperature is brought about

without the use of expensive or complicated apparatus and with practically no danger of clogging the system. While this method has been tried out only in the laboratory, and some of the analytical data are not altogether satisfactory, the results obtained prove that the principle is good, and that the process if worked on a factory scale would probably be commercially successful.

In a review of the patent literature on the subject an apparatus was found which is somewhat similar to the one herein described. This United States patent (No. 446060) was taken out by E. and J. Delplace in 1891, and consists of a lead chamber having the shape of a ring with a sector cut out. The chamber is provided with two gas inlets at unequal distances from the centre, and contains at intervals distributing pipes leading from the upper part to the lower part of the chamber, so that the hot gases can be more thoroughly mixed with the cooler. The inventors state that in such a chamber the constant change in the direction of the gases and their impinging on the sides of the chamber cause a thorough mixture and a condensation of the acid formed. In this patent the right is reserved to vary the shape of the chamber provided the gases are led through a circular route.

The main objections to the above apparatus in the opinion of the writer are, first, that the chamber as described is of such a size that there must be spaces therein where the gases are relatively inactive; second, the pipes for conveying the hotter gases from the upper to the lower part of the chamber would hardly accomplish this unless they were the only route provided for the passage of the gases, and this according to the specifications is not the case; third, the use of pipes within the lead chamber, unless they are cooled, is always objectionable because of their excessive corrosion and the serious consequences resulting therefrom; fourth, a chamber of the shape described occupies an enormous amount of ground space. Where land values are high this entails a large outlay for a factory site as well as an expensive building to house the chamber.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 25, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE Bakerian Lecture was delivered by Prof. G. C. BARKLA, F.R.S., on "*X-Rays and the Theory of Radiation.*"

CHEMICAL SOCIETY.

Ordinary Meeting, May 4, 1916.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Messrs. Walter Harris Coffin (April 10), Cornelius Hanbury (April 11), and Frederick Wallis Stoddart (April 15).

Certificates were read for the first time in favour of Messrs. George Arthur Alder, 45, Lothian Road, Middlesbrough; Frederick Hartridge Branson, Myrtle Cottage, Talbot Grove, Roundhay, Leeds; George Van Barneveld Gilmour, B.Sc., 10, Herbert Road, Southall, Middlesex; William George Ramsay, B.Sc., Beechcroft, Hazlemere, High Wycombe, Bucks; Simon Solomon, 111, Sandringham Road, Dalston, N.E.; Fred Taylor, Womersley Road, Knottingley, Yorks; Cecil Francis Tidman, B.Sc., 1, Rockcliffe Terrace, Carlin How, Yorks.; Arthur Rokeby Ward, Hazleden Villas, York Street, Wakefield.

Messrs. O. L. Brady and H. King were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Ernest Arthur Bearder, M.Sc.; Nowrosji Maneckji Bhathena; Hanns Bleuler, Ph.D.; William Arthur Graham Burton; John Archibald Clark; Cyril Stanley Dawes; Ernest John Dobbs; Robert Ferguson; Geoffrey Edwin Foxwell; William Edward Garner, M.Sc.; John Henry Gill; Harold Cecil Greenwood, D.Sc.; Edward Owen Jones, B.Sc.; Nikolai Ivanovitch Kursanov; Edgar Lewis; Hans Hugo Herbert Lorenz, M.A.; Hugh Findley MacLachlan; James Baird MacLachlan; Arthur Marsden; Charles Ainsworth Mitchell; Bangalore Pasupulcti Balakrishna Naidu, M.B., Ch.B.; Joseph Bernard Oesch, Ph.D.; Hubert Ernest Page; George Humphrey Pierson; Leonard William Raymond, B.A., B.Sc.; Conrad Howard Rogers; Alexej Evguenievitch Tschitschibabin; Ralph Winton West.

The following papers were read:—

"A Space Formula for Benzene." (Part II.). By J. N. COLLIE.

"3-Phenanthrol-4-aldehyde." By J. W. SMITH.

Extraordinary General Meeting, May 11, 1916.

THE meeting was summoned "to consider the question of the removal of the names of nine alien enemies from the list of Honorary and Foreign Members of the Society."

The following resolution was proposed by Dr. G. T. MOODY and seconded by Col. CHARLES E. CASSAL.

"That in view of the many contraventions of international agreement which have marked the conduct of the war by our enemies, this General Meeting hereby removes from the roll of Honorary and Foreign Members of the Chemical Society the names of A. von Baeyer, T. Curtius, E. Fischer, C. Graebe, P. H. von Groth, W. Nernst, W. Ostwald, O. Wallach, and R. Willstätter."

Prof. W. H. PERKIN then moved as an amendment:—

"That judgment be suspended until after the war, in accordance with the resolution of the former Council."

This was seconded by Sir WILLIAM TILDEN, and after further discussion was put to the meeting and carried by 93 votes to 91.

Circumstances prevented the amendment being put to the meeting as a substantive motion, and the meeting was then adjourned.

Ordinary Meeting, May 18, 1916.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Arthur John Dickinson (May 4) and Edward Jackson (April 16).

The PRESIDENT referred to a communication received from the Committee of the van't Hoff Memorial Research Fund. The amount available for distribution during 1916 is about £100. A Committee, consisting of Prof. A. F. Hollemann, Prof. S. Hoogewerff, Prof. A. Smits, and Prof. E. H. Büchner (Secretary), has been appointed to award grants. Applications should be sent before November 1, 1916, by registered post, to "Het Bestuur der Koninklijke Akademie van Wetenschappen; bestemd voor de Commissie van het 'van't Hoff-fonds' Trip-penhuis, Kloveniersburgwal, te Amsterdam," and applicants are requested to submit a detailed account of the manner in which they propose to expend the grant.

Papers embodying the results of the Research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the Research must be forwarded to Committee.

Mr. L. W. Raymond was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Joseph George Clark, 64, Hewitt Road, Harrin-

gay, N.; Samuel Harold Green, St. Neots Villas, Lelant, Cornwall; Frederick William Jackson, B.Sc.; The Laurels, Langley Green, Birmingham; William Alexander Whittton, B.Sc., The Grammar School, Ross-on-Wye.

The following Certificates have been authorised by the Council for presentation to ballot under By-law I. (3):—Peter Petrovitch Lasazeff, Royal Technical School, Moscow; David Christophorovitch Zavriev, Petrograd Street 10, Tiflis, Russia.

Prof. F. GOWLAND HOPKINS, M.A., D.Sc., F.R.S., delivered a lecture entitled "Newer Standpoints in the Chemical Study of Nutrition." After the discussion, in which Prof. H. E. Armstrong, Prof. A. Harden, Dr. R. H. Aders Plimmer, and Dr. F. L. Pyman took part, a vote of thanks to the Lecturer was proposed by the PRESIDENT and carried unanimously.

PHYSICAL SOCIETY.

Ordinary Meeting, May 26, 1916.

Prof. C. V. BOYS, F.R.S., President, in the Chair.

A PAPER entitled "*The Correction of Chromatic Aberrations when the External Media are Dispersive*," was read by Mr. T. SMITH.

When one of the external media of a lens system is dispersive it is not possible to ensure the absence of differences in the size and position of images of all objects formed by length of different wave-lengths. The degree to which correction can be carried is investigated, and formulæ are given by which the power and position of the external surfaces of a system can be found when the type of correction to be adopted is given.

A paper entitled "*Note on the Use of the Autocollimating Telescope in the Measurement of Angles*" was read by Mr. J. GUILD.

The measurement of angles by means of the autocollimator resolves itself into the measurement of the distance between two images produced in the focal plane of a micrometer eye-piece. In most cases the light forming these images passes through portions of the object glass on opposite sides of a diameter. It is shown that, when this diameter is perpendicular to the direction of the displacement to be measured, uncertainty and error are introduced on account of any residual spherical aberration of the object glass and the depth of focus of the telescope. One or two particular cases are discussed in which it is shown how this may be obviated.

DISCUSSION.

Dr. R. S. WILLOWS asked why the Abbé type of autocollimating eye-piece, such as is used on Pulfrich refractometers, &c., was not employed in the arrangement described in the paper.

THE AUTHOR explained that there was a difficulty in adapting this method of illumination to a micrometer eye-piece.

A paper entitled "*The Viscosity of Colloidal Solutions*" was read by Mr. EMIL HATSCHKE.

The author, in reply, to some remarks made by Mr. W. B. Hardy in the course of his Guthrie lecture, points out (a) that no viscosity formula can cover the stage of gel formation, since the change from a liquid with only slight anomalies to a system having many properties of an elastic solid necessarily precludes this, and (b) that the formula given by Einstein, and independently by himself, for the viscosity of a suspension of rigid spherical particles, does not in any event apply to systems such as discussed by Mr. Hardy, which belong to the class known as emulsoids. In these both phases are quite generally assumed to be liquid, and an expression for the viscosity of such systems was deduced by the author in 1911, from a consideration of the deformation which a homogeneous polyhedral structure must undergo when sheared. The expression contains only the viscosity of the system and

the phase ratio, but neither the interfacial tension of the phases nor the viscosity of the disperse phase. It can be tested directly for emulsions of two immiscible liquids; in the case of emulsoids, where only the weight of dispersed substance is known, some assumption has to be made about the relation between the volume of disperse phase formed—i.e., the degree of hydration or solvation—and the weight dissolved. The simplest assumption, that this ratio is constant, has been tested by the author, and by Harriette Chick, for a number of sols, and is found to hold good over a considerable range. The formula has also been tested by F. Kirchhof in a different way, by comparing the degree of solvation—i.e., the amount of solvent taken up by the disperse phase in different solvents—with the amount of the solvent taken up by the substance (indiarubber) in the swelling which precedes dispersion. Remarkable agreement both in the order and in the absolute amounts in different solvents was observed.

DISCUSSION.

Dr. A. GRIFFITHS said he was in emphatic agreement with the conclusion at the end of paragraph two. He mentioned the case of a gelatin which would not run through a capillary tube, but which could be made to do so when broken up by stirring with a stick. He thought experiments on rigidity as well as viscosity should be made.

The AUTHOR, in reply to a remark by the President, stated that accidental double refraction was sometimes observed in the liquid phase.

NOTICES OF BOOKS.

A Class-book of Chemistry. By G. C. DONINGTON, M.A. Part IV., Metals. London: Macmillan and Co., Ltd. 1916. Pp. vii. + 133. Price 2s.

THIS book contains an expansion of the last two chapters of the late Mr. Donington's "Class-book of Chemistry," prepared by Dr. T. M. Lowry and Dr. P. C. Austin. Many teachers, who had used and highly appreciated the original work, found that the treatment of metals contained therein, although admirable as far as it went, was insufficient for some purposes; for example, for the use of candidates for such examinations as the Oxford and Cambridge Locals, and in response to their wishes this new part has been written. The Class-book is well known as one in which the best features of the older type of descriptive text-book were combined with those in which "research" methods are exclusively adopted, and this further part maintains the high level of the original book and will undoubtedly be warmly welcomed by teachers. A short account is given of the general properties of the metals, and also a chapter upon the classification of the elements according to the Periodic System. All the common metals are treated, more space being given to those which are of technical importance, and the class-book contains a complete course of inorganic chemistry, representing the maximum amount which could be covered by the average schoolboy in a secondary school.

The Dynamical Theory of Gases. By J. H. JEANS, M.A., F.R.S. Second Edition. Cambridge: The University Press. 1916. Pp. vi. + 436. Price 16s. net.

THE second edition of this book has been so much enlarged that it may be regarded as having been almost re-written; the plan, however, of separating the mathematical and physical parts as far as possible has been preserved. The Quantum Theory, which has been developed almost entirely since the last edition appeared, is briefly summarised in the last chapter, the author believing, no doubt rightly, that for the present an extended discussion would be out of place in a book of this kind. As far as it goes, the treatment of the theory could not be surpassed for clearness, and the second edition of the book will be as highly valued as the first for its admirable exposition of

the Kinetic Theory of Gases. The application of the principles and results of the theory to problems connected with the atmosphere leads to the discussion of the nature and properties of the atmospheres of planets other than the earth, and an investigation of the question of the dissipation of planetary atmospheres, and various problems of aerostatics, and the chapters grouped together as dealing with "Various Problems and Applications" will probably prove specially interesting to the non-mathematical reader.

Degenerate Germany. By HENRY DE HALSALLE. London: T. Werner Laurie, Ltd. Pp. vii. + 260. Price 2s. 6d. net.

THIS book contains a terrible indictment of the German people, and in its pages are to be found many facts that should be known to the civilised world. The social and moral degradation of twentieth century Germany, the debasement of its literature, and the low ebb of its religion are eloquently described, and the author makes out a very strong case against Germany's so-called Kultur. The German educational system and its scientific work are not discussed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 17, April 25, 1916.

Manganese in some Springs connected with the Central Massif, and in some Stations of the Plain of Languedoc.—F. Jadin and A. Astruc.—The authors have found that the waters of the Central Plateau are rich in manganese, always containing considerably more than a tenth of a mgrm. per litre. In the Plain of Languedoc the amounts of manganese found in the waters vary from 0.4 to 0.001 mgrm. per litre, and the data obtained confirm the conclusions, already reached, as to the amounts of manganese in French spring waters.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 5th inst.; Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. John Quiller Rowett was elected a Member of the Royal Institution.

Metropolitan Water Board.—The December report of the Metropolitan Water Board contains the results of the chemical and bacteriological examination of the London waters for the twelve months ending December 31, 1915. A short summary is included of the special researches, chiefly bacteriological, carried out between 1905 and 1915, and a statement is given of the conclusions which may be drawn from the work of the Board. The great value of storage has been demonstrated beyond dispute, although it is often attended by the troublesome development of algae, about which so far not very much is known.

MEETINGS FOR THE WEEK.

THURSDAY, 15th.—Chemical, 8. "Studies on the Walden Inversion—Part IV. The Kinetics and Dissociation Constant of Phenylbromoacetic Acid," by G. Senter and S. H. Tucker. "Reactivity of the Halogens in Organic Compounds—Part IX., Interaction of Alkalies and Alkali Bromoacetates and Bromopropionates in Ethyl Alcoholic Solution," by G. Senter and H. Wood.

FRIDAY, 16th.—Physical, 5. "Method of Measuring the Pressure of Light by means of Thin Metal Foil," by G. D. West. "Viscosity of Suspensions of Rigid Particles at Different Rates of Shear," by Edith Humphrey and E. Hatschek. "Experiments with Mercury Jet Interrupters," by Capt. C. E. S. Phillips. "A Correction of Some Work on Diffusion by Dr. A. Griffiths and others," by A. Griffiths.

THE CHEMICAL NEWS

VOL. CXIII., No. 2951.

THE PREPARATION OF ETHYLENE DIBROMIDE.

By E. B. R. PRIDEAUX, M.A., D.Sc.

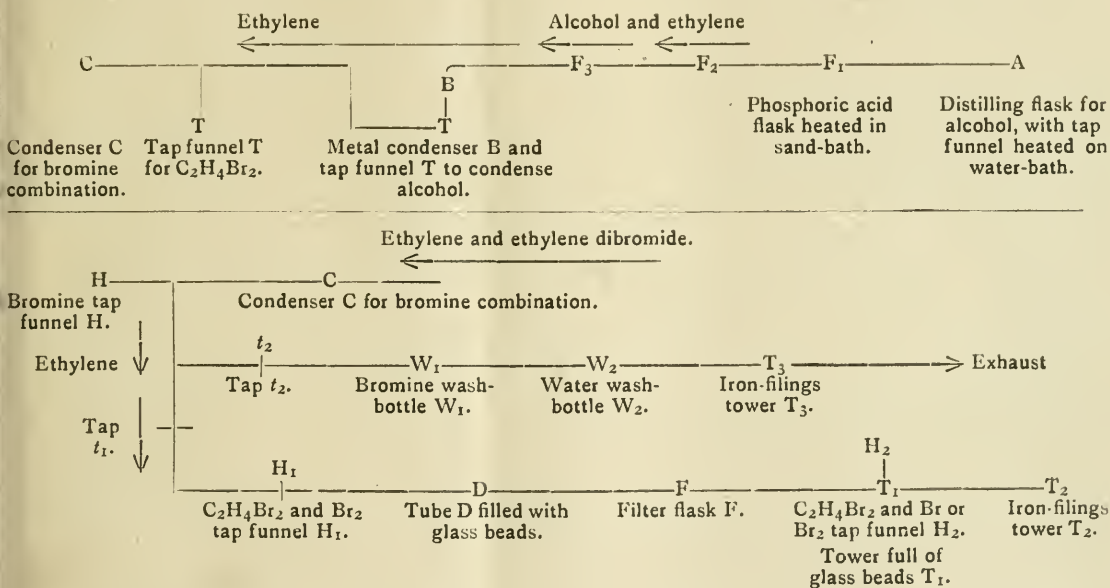
WHILE large quantities of ethylene dibromide were being required in the laboratories of University College, Nottingham, it was suggested to the author of this paper by Prof. Kipping that the combination of the C_2H_4 and the Br_2 might be continuously and easily effected by the principle of counter-currents. In carrying out this idea a modification of the usual method for preparing the C_2H_4 also suggested itself.

The results obtained up to the time when the work was discontinued seemed to show that the process offers certain

of which it met the current of bromine run in from H. The condenser should make only a small angle with the horizontal, and not more than a few cc. of the ethylene dibromide should remain in the outlet. Glass beads are unnecessary and retain too large a volume of liquid in the condenser. It was found best to construct the whole apparatus in such a way that no hydrostatic pressures impeded the flow of the gas.

On account of unavoidable fluctuations in the supply of ethylene and of bromine it was necessary to work with excess of one or the other. If the latter, then only a water wash-bottle and an iron filing tower would be required for the absorption of this. But ethylene dibromide containing bromine is produced, and this cannot be decolorised by bubbling the ethylene through the liquid in T, but has to be shaken out with sodium hydroxide. So it was decided to keep the ethylene in excess, this being subsequently absorbed. It was first passed down a tube, D (a dry condenser was used), which is filled with glass beads moistened with a bromine-containing sample of ethylene dibromide produced in the wash-bottle, W_1 .

(NOTE.—The counter-current principle could of course have been adopted here also).



advantages which are worth noting by others who require to prepare continuously large quantities of the compound.

The following conditions should be fulfilled by a good process:—

1. Conversion of a large proportion of alcohol into ethylene.
2. Complete conversion of ethylene into the dibromide.
3. Preparation of the dibromide free from bromine in one operation.
4. Conversion of all the bromine into dibromide. The least possible amount should combine with iron, or escape. The apparatus should be so designed that there is seldom a necessity for disconnecting parts in which free bromine is present.
5. Connected with the last condition is that of continuous working. The process should not be interrupted when alcohol and bromine are added or ethylene dibromide is withdrawn.

The current of ethylene, prepared as described below, was freed from alcohol by passing through the metal condenser, B. The gas then passed through the large two-necked tap funnel up into the condenser, C, near the top

The last traces of the gas are then removed by the tower, T_1 , containing beads moistened with the same liquid or a little pure bromine. A similar tower, T_2 , contains wet iron filings to prevent diffusion of bromine into the air.

In the preparation of the ethylene, instead of running the alcohol straight into the phosphoric acid, alcohol vapour was passed through the phosphoric acid.

The supply of alcohol in A was heated on a constant level water-bath. The heating must be finely regulated and the gas flame well protected from draughts.

The vapour passes through phosphoric acid contained in three flasks fitted with thermometers and heated on sand-baths. By this means it was thought that less of the alcohol would escape conversion into ethylene. The gas can, however, be produced more rapidly by connecting the flasks in parallel. Care must be taken not to run fresh alcohol too quickly into the flask. If this is done and the phosphoric acid sucks back, the remedy is to close t_1 , open t_2 , and connect the second iron filing tower with the water-pump.

The chief trouble was caused by the irregularity of the

delivery of bromine from H through a tap of rather fine bore.

A better tap might be used, or this part of the apparatus might be improved by delivering bromine vapour at a high velocity from a tube of capillary bore. A greater head of bromine in the tap funnel would also be an advantage.

The apparatus would then run continuously with very little attention, and would not need to be disconnected except in order to renew perished paraffined corks or hardened rubber. The objects set forth at the beginning of this note were fairly well attained, with the exception of 1.

A good deal of the alcohol escapes dehydration. This is not a serious objection, however, for it should be possible to return the condensed alcohol directly to A.

In conclusion I have much pleasure in acknowledging the able assistance of Mr. N. Chambers, who has worked with the apparatus and suggested improvements.

University College, Nottingham.

ON "THE HISTORY OF THE SAFETY-LAMP."

By Prof. F. W. HARDWICK, M.A.,

and
Prof. L. T. O'SHEA, M.Sc.

Introduction.—The paper is divided into fourteen sections, the first of which is introductory. Sections II., III., and IV. deal with the early history of fire-damp and its occurrence in mines, and the lighting of mines previous to the introduction of the safety-lamp.

Sections V., VI., VII., and VIII. deal with the parts played by Clanny, Stephenson, and Davy in the invention of the safety-lamp.

Section IX.	deals with the period	1816 to	1835
Section X.	" "	1836 "	1843
Section XI.	" "	1844 "	1866
Section XII.	" "	1867 "	1879
Section XIII.	" "	1880 "	1887
Section XIV.	" "	1888 "	1913

Two appendices are added, namely:—

I.—List of safety-lamps described in Appendix XXIV. to the Final Report of the Royal Commission on Accidents in Mines of 1886.

II.—Some publications relating to the safety-lamp and to the early history of fire-damp.

The earliest references to the nature of fire-damp appear to occur in the latter part of the seventeenth century. From these it is evident that the risk of its ignition and explosion were known, and it was recognised that ventilation (to keep the air very "quick") was a means of prevention of these dangers. The recognition of the presence of fire-damp by means of the candle-flame was also known. No remedy other than ventilation appears to have been suggested until about 1730 or 1750, when the flint-and-steel mill was invented. This invention is attributed to Mr. Carlisle Spedding, of Whitehaven. The use of flint and steel in the presence of fire-damp is mentioned by Sir James Lowther in 1733, and Mr. John Buddle in 1813 gave a full description of the flint-and-steel mill. This instrument, however, did not give immunity from explosion. An explosion at Wallsend in 1785 was stated by Mr. Buddle to have been traced to the use of the steel mill, and he also affirmed that, although he had witnessed an explosion from the sparks emitted by the instrument, yet "the inflammable air has frequently fired at the sparks of the steel mills, but only when they are played near the place where the hydrogen gas is discharged." Matthias Dunn also asserted that explosions were originated by the flint-and-steel mill. Other attempts to avoid the use of naked lights in presence of fire-damp were made, and Von Humboldt describes a lamp invented by him in

which a candle would burn supplied with air from an air-reservoir. The use of phosphoric lights, fish in a state of incipient putrescence, Amadou (or fungus tinder), and other schemes were suggested, whilst sunlight was directed down the shaft by mirrors, and proposals were made at a later date to reflect the light into the workings.

Some progress was also made in respect of the knowledge of the properties and composition of fire-damp. Some investigators recognised its similarity to hydrogen gas, and were aware that it was heavier than hydrogen, but lighter than air, and although Volta pointed out the differences between fire-damp and hydrogen as early as 1776, and Berthollet proved that it contained both carbon and hydrogen in its composition, still fire-damp continued to be spoken of as "hydrogen." In 1805 Dr. William Henry distinguished between marsh-gas and olefiant gas. The occurrence of fire-damp in coal-mines was, however, not understood at this date, and in many instances its presence was attributed to the decomposition of water by iron pyrites, or to the decomposition of water by the coal with separation of the hydrogen.

The years 1812 and 1813 were important in the history of the safety-lamp. On May 25, 1812, an explosion occurred at the Felling Colliery. In consequence of this explosion, the Rev. John Hodgson, the incumbent of Jarrow and Heworth, and Mr. James John Wilkinson took steps which eventually resulted in the formation on October 1, 1813, of the "Society in Sunderland for Preventing Accidents in Coal-mines." This society had, as patron, His Grace the Duke of Northumberland; there were sixteen vice-presidents, with Sir Ralph Milbanke, Bart., as president, and Mr. W. Burn as secretary. In addition, there was a permanent committee of twenty-eight, among whom were the Rev. Robert Gray, the Rev. John Hodgson, William Reid Clanny, James John Wilkinson, John Buddle, and Matthias Dunn. This society was most assiduous in its endeavours to promote the objects for which it was formed, and it was due to its efforts that the safety-lamp was introduced at this period. Among those who, at the time when the society was formed, were actively engaged in endeavouring to discover some safe means of lighting coal-mines were William Reid Clanny and George Stephenson, and the society, apparently influenced by Mr. Buddle's expressed opinion that nothing further could be done to prevent explosion by the application of mechanical agencies, that the only remedy lay in the discovery of some chemical method for rendering fire-damp harmless, as it was discharged, and that it had to look to scientific men for assistance in providing "a cheap and effectual remedy," eventually determined to apply to Sir Humphry Davy for assistance.

The work accomplished by the society in connection with the movement of the safety-lamp entitled it to be gratefully remembered by all interested in coal-mining.

Dr. Clanny.—William Reid Clanny was born in 1776 at Bangor, County Down, Ireland. He entered the medical profession, and eventually settled down in practice at Bishop Wearmouth, near Sunderland. In 1810 his attention was drawn to the subject of explosion of fire-damp in collieries. He invented a number of lamps, among which is the well-known Clanny lamp. On May 23, 1813, he contributed a paper on his newly-invented lamp to the Royal Society.

Clanny's first lamp (the "Blast" lamp) consisted of a lantern with cisterns of water above and below the light. Air was forced in by means of a bellows, so that it bubbled through the water in the lower cistern whilst the products of combustion escaped through a chimney at the top, the open end of which was narrowed and bent over so as to dip beneath the surface of the water in the upper cistern. This lamp was tested on the surface on October 16, 1815, and underground on November 20, 1815. The construction of the lamp was subsequently modified; the water cisterns were abandoned, the oil in the oil-vessel was used to seal the inlet of the air, and the outlet consisted of a vertical chimney that tapered to a fine point.

* Abstract of a paper read before the Institution of Mining Engineers, June 8, 1916.

His second lamp was exhibited to the Sunderland Society in December, 1816, was described before the Royal Society of Arts on April 2, 1817, and was known as the "Steam" lamp. Air passed in through a tube in the bottom of a lamp, and was conducted through an extension of the tube to a point high up in the lamp. Above the oil-vessel and flame, and situated about the middle of the lamp, was a water reservoir. The water in the reservoir was boiled by the heat from the oil-flame. The air was conducted below the oil-vessel by two tubes, and then passed up the sides of the cistern, where it mixed with steam from the boiling water, and finally escaped through the chimney.

A third lamp was the "Gaslight" lamp, which was stated to have been designed to burn fire-damp in lieu of oil in an atmosphere charged with gas. It was similar in construction to the steam lamp.

These early examples of Clanny's lamps show the important part that Clanny took in his attempt to reduce the dangers arising from the use of naked lights, and in 1843 the South Shields Committee for Investigating the Causes of Accidents in Coal Mines expressed their opinion of the value of his labours as follows:—

"Dr. Clanny, in this country, appears to have been the first man of science that conceived it possible to enter into a contest with this destructive element (fire-damp), and, sustained by his unwearied philanthropy, has never ceased for thirty years to devote his talents and exertions to mitigate the horrors consequent upon its explosion. A life so spent, it is to be hoped, will not be allowed to pass without some mark of respect from his country, or of gratitude from those he has laboured so much to benefit."

George Stephenson.—George Stephenson, born on June 9, 1781, at Wylam, near Newcastle-upon-Tyne, was, at the age of fourteen, appointed assistant fireman at Dewley Burn Colliery, and engineer at Killingworth Colliery in 1812.

The idea of his first lamp ("The Tube and Slider" lamp) was conceived from experiments made on blowers that he met with in the Killingworth Pit. He found that the "Burnt Air" from five or six candles held to windward of an ignited blower would extinguish the flame. Further, that when fire-damp was ignited, an appreciable time was necessary for the flame to travel from one point to another, and his idea was that if the upper part of a lamp could be charged with burnt air, whilst the fire-damp was admitted below in small quantity and burnt as it came in, then the burnt air would prevent the explosion from travelling upwards, and the velocity of the entering current would prevent it from passing downwards. In the "Tube and Slider" lamp air was admitted through a tube $\frac{1}{2}$ inch in diameter, and passed from the centre of the bottom of the lamp to the centre of the wick; the bottom of the tube could be wholly or partly closed by a valve or shutter, and so the admission of air regulated. This lamp was tested on October 1, 1815, at Killingworth Colliery. Subsequently, Stephenson undertook some experiments on fire-damp and tubes, which decided him to substitute three tubes for the single air-inlet tube, and he constructed his second, or "Tube" lamp, in which the air was admitted through three tubes $3\frac{1}{2}$ inches long and $\frac{3}{32}$ inch in diameter; the air passed from the bottom of the lamp through the oil-vessel, the upper ends of the tubes being inclined towards the wick. This lamp was tried at Killingworth Colliery on November 4, 1815. Subsequently, Stephenson decided that to admit air into the lamp through capillary tubes would be a better method, but afterwards he decided to adopt smaller holes drilled in a plate, and constructed his third lamp, into which air was admitted through holes in the side of the oil-vessel, then through small holes from $\frac{2}{32}$ to $\frac{1}{32}$ inch in diameter into a space between two plates, whence the air issued to the flame through a set of holes $\frac{1}{32}$ to $\frac{1}{16}$ inch in diameter punched in a metal ring. This lamp was tried underground on November 30, 1815. In the final form of Stephenson's lamp, the punched plate was replaced by a gauze cylinder, which surrounded the glass

cylinder; air was admitted through small holes in the ring to which the standards are fixed, or in a flange just above the ring. It has not been possible to ascertain the date when the wire-gauze was substituted for the punched plate.

Sir Humphry Davy.—Sir Humphry Davy was born near Penzance on December 17, 1778. He was educated at the Penzance Grammar School, and was eventually apprenticed to Mr. J. B. Borlase, a surgeon and apothecary. He devoted his attention chiefly to chemistry, and in 1798 was appointed Superintendent in the laboratory of the Pneumatic Institute at Bristol, where he investigated the properties of various gases, among them carburetted hydrogen. In 1801 he joined the Royal Institution as Assistant Lecturer in Chemistry, Director of the Laboratory, and Assistant Editor of the journals of the Institution, and on May 31, 1802, was appointed Professor. He was elected a Fellow of the Royal Society in 1803, was Secretary of that Society from 1807 to 1812, and was elected President on November 30, 1820. He was knighted in 1812, and created a Baronet in 1818. On resigning his Professorship at the Royal Institution, he was elected Honorary Professor of Chemistry. He died at Geneva on May 29, 1829.

It was in August, 1815, that Davy met the Sunderland Committee, and after learning the conditions under which coal was mined and paying visits to the Hebburn and Wallsend Collieries he returned to London and commenced his investigations into the nature of fire-damp, which eventually led to the invention of his lamp. On November 9, 1815, he read a paper before the Royal Society on "The Fire-damp of Coal Mines and on Methods of Lighting the Mines so as to prevent Explosion." In this he gave an account of his investigations into the explosive properties of fire-damp and the passage of flames through glass and metallic tubes. In his paper he stated:—

"It is evident that to prevent explosions in mines it is only necessary to use air-tight lanterns, supplied with air from tubes or canals of small diameter, or from apertures covered with wire gauze placed below the flame through which explosions cannot be communicated and having a chimney at the upper part on a similar system to carry off the foul air, and common lanterns may be easily adapted to the purpose by being made air-tight in the door and sides, by being furnished with the chimney, and the system of safety apertures below and above."

In the paper three lamps are described; they appear to have been lanterns of thin plate with four glass plates in the side. In the first lamp air entered below the flame through a number of tubes one-eighth of an inch in diameter and one and a-half inches long, and the products of combustion escaped through a chimney composed of two open cones protected by a plate containing many small apertures. In the second lamp both inlet and outlet were protected by "safety canals" consisting of concentric metallic cylinders, one within the other, and separated from one another by annular spaces from $\frac{1}{32}$ to $\frac{1}{16}$ inch wide and $1\frac{1}{2}$ inches long. The inlet and outlet of the third lamp was protected by brass-wire gauze $\frac{2}{32}$ inch thick, having apertures not more than $\frac{1}{32}$ inch. A little more than a month later—namely, on January 1, 1816—Davy announced to Dr. Gray his important discovery of the use of the gauze cylinder, and communicated his discovery to the Royal Society in a paper on January 11, 1816. In this paper he describes his invention as follows:—

"This invention consists in covering or surrounding the flame of a lamp or candle by a wire sieve; the coarsest that I have tried with perfect safety contained 625 apertures in a square inch, and the wire was $\frac{1}{16}$ of an inch in thickness, the finest 6400 apertures in a square inch, and the wire was $\frac{1}{32}$ of an inch in thickness."

The first Davy lamps seem to have been tried at Hebburn Colliery on January 9 and 17, 1816. Davy recommended the use of iron-wire gauze composed of wire from

$\frac{1}{16}$ to $\frac{1}{8}$ of an inch in diameter and uncovered with any easily combustible metal; that in proportion as the inflammability of the gas increases the apertures should be smaller and the radiating surface greater, and that several gauzes superposed might be necessary for continuous explosive mixtures. He pointed out that no aperture should be allowed in the lamp and the precaution of supplying a short gauze cap over the top of the main gauze cylinder. He also gave dimensions for the cubic contents of the lamp, recommending that the lamp should be from eight to ten inches high and from two to two and a-half inches in diameter. Davy appeared to be aware of the limitations to the safety of his lamp, especially in currents of explosive gas, and recommended the use of twilled gauze or the protection of the gauze by a glass cylinder above the flame or a tin screen outside the gauze. On September 6, 1816, he visited Wallsend Colliery and performed experiments with his lamps, and in pointing out the lessons to be learnt said:—

"Now, gentlemen, you see the nature of the danger to which you are exposed in using the lamp, and I caution you to guard against it in the manner I have shown you. This is to show the only case in which the lamp will explode, and I caution you and warn you not to use it in any such case when you can avoid it without using the shield."

There is little doubt that Clanny considered himself the inventor of the first safe lamp, and a regrettable controversy arose towards the end of 1816 as to whether Stephenson or Davy was to be regarded as the first inventor of the safety-lamp. It is not necessary to go into the details of the controversy, but in regard to the merits of these two inventors Stephenson deserves great credit for his work. Unacquainted with the principles of chemistry and devoid of proper apparatus for experimentation, he was yet able to produce a lamp which seems to have been safe under the conditions for which it was designed. But to Davy's work the mining community is indebted for the safety-lamp as it exists to-day; not only did he invent a lamp which was within limits safe, but he laid down the principles of safety which have been followed and confirmed by subsequent investigators.

About the same time lamps were devised by Chevrémont, John Murray (Lecturer on Chemistry at Hull), and R. W. Brandling. All these were similar, and consisted of enclosed lamps connected with long tubes through which air free from fire-damp could be brought from a distance.

Period 1816 to 1835.—The Davy and Stephenson lamps came into use shortly after their invention, and in 1818 the Davy was used in the North of England, Whitehaven, and Wales. It was also introduced into France, Belgium, and Germany. It was during this period that distrust arose as to the safety of the Davy lamp when exposed to currents of explosive mixtures other than those moving with low velocities. Davy had foreseen the danger and had suggested precautions that should be taken. There appears to have been a feeling of disappointment that since the introduction of the safety-lamps mortality due to accidents from fire-damp had increased. In 1835 a Select Committee on Accidents in Mines was appointed. The Committee issued its report on September 4 of the same year, in which they stated "that ignorance and a false reliance" on the merits of the Davy safety-lamps "in cases attended with unwarranted risks have led to disastrous consequences," but a more extended use of the safety-lamp was recommended—"in some mines, now lighted by the ordinary means, the use of the lamp ought to be compelled by the owners." Among the lamps brought to the notice of the Committee that of Upton and Roberts is commended. This lamp consisted of a gauze chimney of the Davy type enclosed in a glass cylinder; above the glass and fitting closely on to it was a metal chimney with perforated top. The air entered the lamp through horizontal holes just above the oil-vessel and passed through a double layer of gauze into a cone, by which it was directed on to the flame.

During this period Clanny brought out his fourth or "New" lamp. It was a Davy lamp fitted with telescopic extinguisher in three sections. When pushed up it was held in its place by a thin brass wire and exposed two-thirds of the gauze cylinder. In an inflammable atmosphere the wire fused and let down the shield, leaving only a small scrap of gauze exposed. The flame of the burning gas was extinguished, but a small oil-flame continued to burn. Other lamps introduced during this period were a Mueseler lamp, similar to the Upton and Roberts, lamps by John Martin, John Newman, John Dillon, and the "Refrigerating" lamp of Wood, all of which are briefly described in the paper.

Period 1836 to 1843.—During this period two important investigations into safety-lamps were carried out, namely:—

1. By the Belgian Commission, appointed on April 13, 1836, and

2. By the South Shields Committee, appointed shortly after the explosion at St. Hilda Colliery, which occurred on June 28, 1839.

Both Committees tested safety-lamps from the point of view of safety and issued reports.

The Belgian Commission issued three reports—the first on April 25, 1840; the second on August 31, 1840, and the third on August 30, 1841.

Among the lamps brought before the Commission and tested were the Davy, two lamps designed by Mueseler, the Cambrésy, the Dumesnil, and the Upton and Roberts. In the first report the opinion was expressed that the Davy lamp left much to be desired as regards safety, but that no lamp had been found to take its place except the Dumesnil. In the second report the Commission recommended that the Dumesnil, the Lemielle, and the now well-known chimney lamp of Mueseler be permitted for use provided that their construction and dimensions were the same as the examples placed in the bureau of the *Ingénieurs des Mines*. The third report deals with trials made with the Mueseler lamps in practical working, and confirms the favourable opinion already expressed.

The South Shields Committee tested the following lamps:—The Davy, Stephenson, Clanny (the fourth, fifth, and probably sixth lamps), the Upton and Roberts, and the lamps of Henry Smith, Wm. Martin, and Richard Ayre. The Committee issued their report in 1843, and came to the following conclusions:—

"No mere safety-lamp, however ingenious in its construction, is able to secure fiery mines from explosions, and that a reliance on lamps alone is a fatal error, conducive to those dreadful calamities which they are intended to prevent. . . . The naked Davy is without a complete shield a most dangerous instrument."

"The best description of lamp to be employed is that on the principle of the Improved Clanny and the Mueseler lamps, the latter with a continuous gauze cylinder."

In 1840 Dr. G. Bischof, Professor of Chemistry in the University of Bonn, conducted tests on the Davy lamp and obtained results which agreed with those of Davy.

The lamps tested by the Commissions are shortly described in the paper.

It was during this period that Clanny produced two more lamps (his fifth and sixth) and that Mueseler invented his lamp with the chimney. Clanny's fifth lamp consisted of an internal gauze cylinder, completely surrounded by an impervious metallic shield having glass and lenses in its side and only open at the highest part of the gauze cylinder for about one and a-half inches from the top. There was a half-inch air-space between the cylinder and gauze and air could only enter the lamp after passing over the top of the shield. The lamp was subsequently modified by surrounding the portion opposite the flame with a "thick globular" shield of glass. The sixth lamp was constructed on the plan of the well-known Clanny—namely, with a glass cylinder surrounding the flame and a gauze cylinder doubled at the top fitted closely on to the glass.

The Mueseler lamp tested by the Belgian Committee introduced the chimney inside the gauze and was similar in construction to the unbonneted Mueseler of to-day. The air was taken in above the glass cylinder and had to pass through a horizontal gauze fitted between the top of the cylinder and the chimney. The unprotected glass cylinder surrounding the flame was considered to reduce the safety of the lamps.

Period 1844 to 1866.—During this period three Select Committees were appointed in England between 1849 and 1854 to enquire into accidents in mines. In the reports of Committees appointed in 1849 and 1852 the Davy lamp was criticised on the score of giving defective light and want of security in a strong explosive current. The third Committee pointed out that opinions as to its security varied, but the majority were in its favour.

Inventors appear to have been active in this period, for a considerable number of lamps of both types were introduced. These lamps are referred to in the paper. It is only necessary here to mention the "Jack" lamp, a shielded Davy in which the gauze was protected by a glass cylinder that extended from a short distance above the bottom of the gauze to the bottom of short gauze cap or smoke cap. The "Tin-can" Davy was introduced in 1866, and consisted of a Davy lamp closed in a tin casing with a glass window. In order to improve the light given by the Davy the "Reflecting" lamp was introduced, polished gauze being used and a polished cone being placed below the flame to reflect the light. Two gauze cylinders were used, the inner one "being placed at such a distance from the outer that the fire-damp enclosed between the cylinders (if the flame passes the first) explodes and may extinguish itself."

Period 1867 to 1879.—During this period several investigations on safety-lamps were conducted, the chief of which were those of the North of England Institute of Mining and Mechanical Engineers, of the Belgian Government, of the Société de l'Industrie Minérale in France, and of Messrs. Smethurst and Ashworth. Several new lamps were introduced, but the only new type of lamp was the Gray. The tendency appeared to be to attain a high degree of safety by increasing the complexity of construction. The results of the various investigations showed the insecurity of the Davy in currents exceeding seven to eight feet per second, and in the report of the French experiments the use of the shield (*écran*) is advocated. The Belgian Commission appears to have reported in 1873, and as a result the use of the Mueseler type of lamp was made obligatory in fiery mines. The experiments of Messrs. Smethurst and Ashworth confirmed Davy's results on restricting the diameter of the gauze cylinder.

Period 1880 to 1887.—This period was one of great activity in the investigation of safety in mines. The following Commissions were appointed:—The French Fire-damp Commission of 1878—1882, the Prussian Fire-damp Commission of 1880—1887, the Saxon Fire-damp Commission of 1880, and the British Royal Commission of 1879—1866. In addition experiments were carried out by the Midland Institute of Mining, Civil, and Mechanical Engineers in 1884, by Mr. A. R. Sawyer in 1884—1885, and by the Mining Institute of Scotland in 1886. The reports of these Commissions contributed materially to the growth of knowledge on the subject. The principal results are given in the paper. The importance of the shield or bonnet in increasing the safety was frequently insisted on, but its use was in some cases objected to, as it concealed the gauze from inspection. A very large number of lamps were designed and submitted to tests. It is only possible to mention one of them here—namely, the Marsaut lamp. The first lamp introduced by Marsaut was a bonneted Boty or Clanny, with a chimney, derived from the Mueseler by suppression of the gauze diaphragm. On experimenting with his lamp by raising it into a glass bell containing illuminating gas and then lowering and stopping it opposite to the edge of the bell (in order to cause an internal explosion at the height at which the gas was

mixed with air in suitable proportions), ignition of the gas in the bell took place at nearly every trial. This phenomenon, known as "l'effet Marsaut," occurred with several other lamps when similarly tested. As a result of these experiments Marsaut was led to construct the well-known Marsaut lamp. The gauze diaphragm and Mueseler chimney were replaced by an interior gauze. The large surface of this additional gauze offered means for the better cooling and escape of the gases. The gauzes were protected by a bonnet with holes at the bottom for the admission of air, which was taken in over the glass and had to pass through both gauzes and holes at the top for the escape of the products of combustion. This lamp did not show "l'effet Marsaut."

Period 1888 to 1913.—The most striking features of this period are the large number of official stations erected for testing safety-lamps and the improvement in apparatus used. Stations have been installed in Great Britain, at Eskmeals, in France and in Belgium, and in Westphalia, Silesia, and Saxony in Germany, whilst the Austrian station at Mährisch-Ostrau, used by the Commission 1881 to 1891, appears to have been maintained. Experiments were also carried out at Karwin.

Considerable improvements have been made in the construction of lamps so as to secure strength in the various parts and to facilitate the operations of cleaning and assembling the lamps. Much attention has been given to the question of locking arrangements and magnetic locks have come largely into use. Arrangements for lighting lamps by electric means after they have been assembled have been largely adopted, and in Great Britain, France, and Belgium the efficacy of the bonnet has been fully recognised. In France, Belgium, and Germany the use of internal relighters is very generally approved, but not so in Great Britain. The question of illuminants has also received much attention, and even acetylene lamps have been introduced. Among the more important lamps of this period may be mentioned the Howat "Deflector" lamp, the Ashworth-Hepplewhite-Gray, the Thorneburry, the Fumat, the Body-Firket, the Wolf, and the Hailwood "Combustion-tube" lamp. As the result of recent experiments there has been a tendency to restrict the use of lamps by legislation to "permitted" lamps. This has been done in Great Britain, France, and Belgium. A number of the modern lamps are described in the paper, but it would appear unnecessary to do so here, as their construction is more or less familiar.

The authors have brought their paper to a close at the end of the year 1913 because they consider the history of the safety-lamp as commencing in 1813, although the Davy lamp was not invented until towards the close of 1815. Another reason which decided them to adopt this course has been the difficulty of writing about contemporary events, for since the outbreak of the great European war in August, 1914, the course of events has not been normal, and possibly the development of the safety-lamp has been in consequence arrested.

REMARKS ON THE PRODUCTION OF RADIUM BY THE BUREAU OF MINES, U.S.A.

By CHARLES H. VIOL,
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THE work of the Bureau of Mines in co-operation with the National Radium Institute Company in the production of radium has been given an unusual amount of newspaper publicity. The statements supplied by Dr. Parsons and others interested in the work have often been considerably altered or abbreviated in publication and a great deal of misconception in regard to the work prevails in the public mind. However, we read in the memorandum for the Press, issued several months ago by the Secretary of the Interior, that the Bureau of Mines has "devised methods for the production of radium from

carnotite ore of Colorado and Utah at an average cost of 36,500 dols. a grm., two-thirds cheaper than the market price of 120,000 dols. asked by foreign producers, the new cheaper methods making it more certain that medical institutions will be able to procure a sufficient quantity of radium for the treatment of cancer and malignant growths," &c.

The writer has been interested in the commercial production of radium from carnotite since 1912 and naturally has followed with interest the work of Dr. Parsons and his associates along this line. The problem to be solved was clearly appreciated (Bureau of Mines, *Bull.* 70, 8, 1913) before any work was carried out by the Bureau of Mines, and it was somewhat of a shock to the writer to see how little has been accomplished in the attack on the real problem as testified by the data given in a recent bulletin (Bureau of Mines, *Bull.* 104; "Extraction and Recovery of Radium, Uranium, and Vanadium from Carnotite," by C. L. Parsons, R. B. Moore, S. C. Lind, and O. C. Schaefer). Briefly the problem consists in devising means for economically working up the low-grade carnotite ore, which forms by far the greater proportion of the radium ore occurring in Colorado and Utah. This would involve an economical process for concentrating the ore as well as an efficient chemical method for extracting the radium, uranium, and vanadium from the concentrates, and the refining of these products.

The carnotite ore from the Colorado field will average about 1 per cent or less of uranium oxide, and by hand-picking from five tons of mine ore it is usually possible to sort out a ton of material averaging between 1.5 and 2.0 per cent of uranium oxide. The remaining ore has in the past been considered too poor to ship and so has accumulated on the ore dump, where through weathering, &c., losses of the values result. Up to date the company with which the writer is associated has shipped about 5000 tons of carnotite ore from its mines to the reduction plant at Canonsburg, Pa. Naturally the endeavour has been to ship as high a grade of ore as possible consistent with the quantity requirements, since the ore must be packed to the foot of the trails by burro, then hauled forty to sixty miles by wagon to the nearest railroad, making transportation charges very high. Rich claims have been stripped bare in this effort, and still the average on all of the shipped ore was 1.6 per cent of uranium oxide. Approximately 20,000 tons of low-grade ore were either not mined or not shipped owing to the poor quality of the ore.

(Since the beginning of 1911 the carnotite ore shipped in Colorado and Utah had a uranium oxide content of approximately 200 metric tons. Of this ore about 55 per cent has been treated in the United States and the balance has been shipped abroad. In the earlier years a large proportion of the carnotite ore was shipped abroad by the General Vanadium Company for the recovery of vanadium. The radium is the residue after the extraction of the vanadium was not refined; however, these residues have since been offered for sale, so that the radium will probably be extracted. The total amount of radium in the carnotite ore so far mined and shipped amounts to about 66 grms., and assuming an efficacy of extraction of 70 per cent the recovered radium would be about 46 grms., of which 25 grms. should have been extracted in the United States and about 21 grms. (including General Vanadium Company residues) abroad. This represents the bulk of the world's present supply of radium, since none of the other deposits of radium compare with the Colorado and Utah deposits).

The results so far attained by the Bureau of Mines may be summarised briefly. About 1000 tons of high-grade carnotite ore (2.5 to 2.6 per cent U_3O_8) have been treated (without concentration) by a method (extraction with concentrated nitric acid) which is not directly applicable to concentrates, and a fairly high extraction of radium has been attained (85 to 90 per cent). The uranium in the ore has been extracted as crude sodium uranate with an efficiency of about 85 per cent and the vanadium as iron

vanadate with an efficiency of 21.4 per cent. Nearly 5 grms. of radium (element) have been extracted from the ore in the form of raw radium barium sulphates containing about 1 mgrm. of radium per kilogram. of salt, and of this material about half has been worked up to yield radium salts of sufficient purity for the designed therapeutic uses. Nothing essentially practical has been contributed to the art of radium production, and the cost data as given are of no great significance for actual large scale production of radium, since the conditions under which the Bureau of Mines produced the radium were abnormal and cannot be duplicated in present practice on account of the lack of high-grade ore.

(Considering that these investigations were made in part (*Bull.* 104, 13) "to enable the miner and prospector to obtain a just return for the ores" it is hard to reconcile this statement with the pitifully inadequate prices paid to the miners by the National Radium Institute for high-grade ore after the war had cut off the European ore market. Before the war carnotite containing 2 per cent U_3O_8 was sold to French buyers at 3.30 dols. per lb. of U_3O_8 , and offers went as high as 4 dols. for this ore. These prices figure 132 dols. and 160 dols. per ton of 2 per cent ore, and at the same rate would give 178.20 dols. and 216 dols. per ton of ore containing 2.6 per cent U_3O_8 , such as was worked by the Bureau of Mines and shown in *Bull.* 104 in the costs at 96.36 dols. per ton. In addition to the ore mined from the Crucible Steel Mining and Milling Company's claims ore was purchased directly from miners, and for this ore the National Radium Institute paid in one known instance 1.70 dols. per lb. of U_3O_8 in about twenty-five tons of ore f.o.b. Placerville, Colorado, that averaged 3.19 per cent U_3O_8 , or at the rate of 108.46 dols. per ton of ore. For ore containing from 2 per cent to 5 per cent U_3O_8 they offered f.o.b. Denver 2 dols. per lb. of U_3O_8 , or 80 dols. per ton of 2 per cent ore. Freight rate—Placerville to Denver, 6 dols. per ton; Placerville to New York, 11.57 dols. per ton; Placerville to Hamburg or Liverpool, via Galveston, 14.50 dols. per ton. When it was evident that the National Radium Institute was in the field to buy ore the State Commissioner of Mines in Colorado made public announcement advising miners to hold their ore for at least 2.50 dols. per lb. of U_3O_8 in 2 per cent ore and proportionally higher prices for higher grade ore. Yet it is on the basis of the rich ore obtained "for a song" that the Bureau bases its production figures for cheap radium. Consistency seems lacking in the argument that the miner will profit by cheaper radium. It is possible that the various arguments are to apply independently—one to the miners, others for the physicians and hospitals, &c.).

In *Bulletin* 104 there is no summary which would show the total amounts of each chemical required per ton of ore, and there is no cost price stated for the acids and alkalis. The result is that there is no simple way for an outsider to figure costs on the Bureau of Mines process. Furthermore, in figuring the cost of any article it is necessary to add the cost of marketing (which has not been done in the 37,599 dols. per grm. of radium—*Bull.* 104, 117) and a sum for the safe and certain profits on the investment. These charges are indispensable and very considerable items for an article like radium. Indeed, with an uncertain market such as radium has the allowances for these items must be far higher in proportion to the cost of production than on such staples as gasoline, copper, &c., and for these articles the selling price is by no means the cost of production of the most favoured producer.

Average mining costs cannot be estimated by stripping out 800 tons of high-grade ore from one rich claim, nor will the mining of several hundred tons of ore on adjacent claims give an average for the whole Colorado field. In actual practice a great deal of preliminary work must be done before the ore is uncovered, and only in rare cases are considerable bodies of high-grade ore found which would compare with the "Maggie C." claim, from which

the Bureau of Mines secured most of the ore. With rich claims advantageously located, so that little if any packing by burro was necessary, and with the good roads already constructed, it is not surprising if ore costs were low.

Dissolving carnotite in strong nitric acid was the analytical method used more than ten years ago in the quantitative determination of radium in this material. This is the basis of the Bureau of Mines method and when applied to rich ore ground to 20 mesh gives an efficient extraction. The same method, however, will not apply to the 200 mesh concentrates, since the finely powdered silica in the concentrates makes it almost impossible to filter the mixture (see also *Bull.* 104, 111). Low-grade ore containing 0.8 to 1 per cent U_3O_8 must be concentrated. A 2.5 per cent U_3O_8 concentrate from such ore is much higher in Mg, Al, Fe, and Ca salts than a straight 2.5 per cent ore and would require more nitric acid than the unconcentrated ore. It is not yet shown that the presence of considerable amounts of gypsum (which frequently occurs with the carnotite and would be found in the concentrates) would not introduce difficulties in the way of a poor extraction should mechanical or other means be found to overcome the filtration difficulty. These are the problems of the practical radium producer which the Bureau of Mines has barely touched, problems of the highest importance for the real conservation of our radium deposits.

Under the agreement made the Crucible Steel Company, which owns the claims that were worked (*Bull.* 104, 8), "agreed that if the National Radium Institute should be formed these claims would be leased to the Institute on a 15 per cent royalty basis under an agreement providing for the return of the uranium and vanadium content of the ore to the company." Vanadium in the form of ferro-vanadium has a high value in the steel industry, and yet the Bureau was satisfied with an extraction process for radium where the vanadium recovery is shamefully low. This is admitted, for we read (p. 107):—"The process described in this bulletin could not be recommended were the recovery of the vanadium in the ore the main object." However, in spite of the contract to deliver to the Crucible Steel Company the uranium and vanadium, we find that little effort was made to extract this vanadium, for (p. 109) "lately on an average 55.5 per cent of the vanadium in the ore remains in the residue and 13.6 per cent remains in the iron-calcium precipitate, while 8.1 per cent appears in the sodium uranate and 21.4 per cent in the iron vanadate. The total average recovery in vanadium, including that from the sodium uranate, is therefore a little less than 30 per cent." No statement is made as to the amount of this material delivered nor as to the opinion of the Crucible Steel Company with regard to the results of the process for uranium and vanadium. Doubtless such a method of extraction could hardly appeal to that company as satisfactory.

As regards the mining and concentration of lower grade ore, *Bulletin* 104, 11, says:—"A separate report on the mining and concentration of radium ores is being prepared and will shortly be published by the Bureau." Dr. Parsons in a lecture at the Chemists' Club in New York, before the New York Section of the Society of Chemical Industry, on December 17, 1915, stated that the concentration experiments were being made using the air separator, the Raymond mill being used. He was not prepared to state results. However, the writer can say, as a result of the experiments of one company, that this mill will not give an economical treatment of low-grade ores, and it can hardly be said that this result is due to lack of experience, since the Raymond separator has been in use by the Standard Chemical Company since the beginning of 1912. In trying this particular apparatus the Bureau of Mines was only borrowing a method already in use.

The National Radium Institute has profited largely by the co-operative agreement with the Bureau of Mines, since the conditions under which the agreement was made were such as to ensure either the delivery of the radium or

the termination of the work if the radium could not be produced. However, it does not require the production of 5 grms. of radium from high-grade ore by a "skimming the cream" method to determine whether or not radium could be produced by the Bureau of Mines, and it is significant that costs were figured on this method rather than on a method involving the use of the average ore. Costs, using the Bureau process and based on normal conditions, would show nearly double the stated cost of production and would of course not verify the earlier assertions of the officials of the Bureau with regard to their process. Having demonstrated the ability to prepare radium it is rather odd that the purposes of the Bureau and the National Radium Institute—namely, the study of the mining and concentration of ores and the working up of the concentrates—has been delayed while radium was being extracted for a private corporation for use (in one instance at least) in a private hospital for private gain. According to *Bull.* 104, 8, such a co-operative agreement is legal and justified in view of similar co-operative work between the Department of Agriculture and farmers, and the Assistant Secretary of the Interior approved of the arrangement. This explanation, however, really does not seem to justify the actual arrangements made, for in the case of the Department of Agriculture the results obtained benefit many others, since the results are general in nature, whereas here a corporation has, through some considerable expense to the Government, profited in securing much valuable material under special arrangements and under conditions which do not offer equal opportunity to all. Ostensibly the purpose of this work by the National Radium Institute is to further the cause of radium therapy—and the production of radium. The results so far have been the exact reverse. The market for radium for therapeutic purposes in America has been killed, since the physician who reads in the newspaper that the Government has produced radium for one-third the present selling price hesitates to buy radium, and as a result of the statements widely spread both by the Bureau of Mines and by the President of the National Radium Institute, to the effect that it is useless to try to cure cancer without the application of comparatively enormous amounts of radium, we find the surgeons and physicians hesitating to venture into the field of radium therapy. The result practically is to confirm the National Radium Institute in a monopoly of radium for therapeutic purposes. Legislation in regard to the Government radium lands is again pending, and it seems more than a coincidence that *Bulletin* 104 should appear with its glitter of cheap radium at this moment.

(In connection with the matter of high dosage it is of interest to note that the London Radium Institute, a charitable foundation not for gain, which has over 2 grms. of radium for application, in the last report of work shows the following amounts of radium element as the highest used in the treatment of those malignant conditions which require heavy dosage:—Cancer esophagus, 61 mgrms.; cancer uterus, 107; cancer bladder, 64.2; cancer breast, 187; cancer thyroid, 225; cancer rectum, 134; cancer prostate, 97; periosteal sarcoma, 86; lymphosarcoma, 225; lymphadenoma, 268; splenic leukemia, 145; fibroid disease of the uterus, 107; mediastinal tumour (patient died suddenly less than two months after treatment), 480. The quantities given are maximum, and more frequently smaller amounts suffice. To the certain knowledge of the writer there are in the United States, besides the hospitals benefited by the radium produced by the Bureau of Mines, three institutions and medical men possessing 200 or more mgrms. of radium element, and besides these there are ten institutions and physicians that possess 100 or more mgrms., and sixteen that have 50 or more mgrms. available. The results in radium therapy reported by these institutions and physicians show that the quality of their work compares favourably with the work in institutions where over a grm. of radium is available, the number of patients treated of course being smaller).—*Journal of Industrial and Engineering Chemistry*, viii., No. 3.

THE DETERMINATION OF VANADIUM BY
CUPFERRON, $C_6H_5N(OH_4).NO$.By W. A. TURNER,
Kent Chemical Laboratory, Yale University, U.S.A.

THE present paper gives the results of experiments begun nearly two years ago on the determination of vanadium by means of cupferron (the ammonium salt of nitrosophenylhydroxylamine). At that time the actual determination of vanadium by this means was not so much sought as its separation from the element uranium. (The use of cupferron for this purpose was suggested by Dr. W. M. Thornton. While this work was in progress two papers by Rodeja have appeared, to which reference will later be made). A large number of experiments carried out for this purpose failed to reveal the proper conditions for a successful separation of these two elements. However, something was learned of the reaction between vanadium and cupferron, and it is with this reaction and its application to the estimation of vanadium that the present paper deals.

Vanadium in the form of its soluble vanadate in slightly acid solution (hydrochloric or sulphuric) gives with cupferron a mahogany-red precipitate. This reaction is so delicate that it may well be used as a qualitative test for a vanadate. If the solution has a low concentration of vanadium a red coloration instead of a precipitate is obtained. A solution containing 0.000004 grm. vanadium per cubic centimetre gives a distinct coloration. Solutions of much lower concentration do not in my experience give the test.

A solution of ammonium metavanadate, prepared by precipitation from a solution of sodium vanadate by means of a saturated solution of ammonium chloride (*Ann. Phys.*, 1831, xcvi., 54) and then washing until free from chlorides, was used for this work. The metavanadate was dissolved in water by constant stirring and gradual addition of concentrated hydrochloric acid.

To obtain the vanadium content of this solution the volumetric method, which involves a reduction of the vanadate by sulphurous acid and then oxidation by a measured amount of standard $KMnO_4$ solution, was used. There was some inconvenience in applying this method because of the fact that the vanadium solution contained hydrochloric acid, which acted upon the $KMnO_4$, giving too high results. This difficulty was overcome with some degree of success by evaporating the weighed portions of vanadium solution with sulphuric acid to remove the hydrochloric acid and then diluting and carrying out the process above mentioned.

In this way the following results were obtained:—

TABLE I.

Exp.	Grms. of NH_4VO_3 solution taken.	Grms. of V_2O_5 found.	Grms. of V_2O_5 per 25 grms. of solution.
1.	25.9374	0.1714	0.1652
2.	25.9846	0.1747	0.1681
3.	25.6772	0.1699	0.1654
4.	25.9426	0.1727	0.1664

These results not being wholly satisfactory in establishing the vanadium content of the solution it was decided to try the apparently simple method of evaporating weighed portions of the solution, igniting the residues, and weighing the amounts of vanadium pentoxide obtained. In this process also the presence of hydrochloric acid is an inconvenience. The results obtained were too low. It was noted that in the ignition some volatile product was formed which was deposited on the cover and the outer edges of the crucible. It is probable that some of the very volatile oxychloride, $VOCl_3$, is formed. An attempt was made to prevent this by evaporating the solution with sulphuric acid and thus remove hydrochloric acid, but under these conditions high results were obtained, evidently due to the formation of a not readily decomposable vanadium sulphate. Simple evaporation and ignition

of the ammonium vanadate solution was finally again resorted to, and by a careful regulation of the heat (the temperature being very gradually increased from the lowest possible flame of a Bunsen burner to the high heat of the Meker burner) the following quite concordant results were obtained:—

TABLE II.

Exp.	Grms. of NH_4VO_3 solution taken.	Grms. of V_2O_5 found.	Grms. of V_2O_5 per 25 grms. of solution.
5.	25.4215	0.1679	0.1651
6.	25.4215	0.1680	0.1652
7.	25.4215	0.1683	0.1655
8.	25.4215	0.1690	0.1662
9.	25.4215	0.1681	0.1653
10.	25.4215	0.1683	0.1655

The mean of these results was taken as the true value and the standard thus established as:—25 grms. solution = 0.1655 grm. V_2O_5 .

The determinations by means of the cupferron solution were carried out as follows:—

Portions of about 25 cc. of the metavanadate solution, accurately weighed, were diluted to about 150 to 200 cc. The hydrochloric acid present in the metavanadate solution was sufficient for the complete precipitation of the vanadium. Not more than 1 per cent acid content (hydrochloric or sulphuric) is needed. Cupferron solution (6 per cent) prepared according to Baudisch (*Chem. Zeit.*, 1911, xxxv., 223) was then added with stirring until a slight excess was present, as shown by the appearance of a white precipitate of nitrosophenylhydroxylamine (formed when cupferron comes in contact with an acid solution). Two or three cc. in excess are added and the precipitate is filtered on paper without delay and washed with a 1 per cent solution of sulphuric acid containing a little cupferron. The precipitate after being allowed to drain on the filter for a time is transferred with the paper to a platinum crucible, dried, ignited, and weighed as vanadium pentoxide.

In this process there are several precautions which should be observed. The precipitate after being filtered on paper is transferred to a large platinum crucible and heated with a small flame to dry the mass and remove volatile substances from the precipitate and paper. This should be done cautiously in order not to produce a heat sufficient to fuse the vanadium oxide. If the attempt is made to hasten the ignition the carbon of the unburned filter may mingle with the fused vanadium oxide, thus delaying the oxidation of the former, which is ultimately accomplished probably more or less at the expense of the latter. At best some of the oxide is likely to become reduced, and must be thoroughly exposed to the action of the air by revolving the crucible held by the tongs in the flame and allowing the fused oxide to flow on the sides. By this means the oxide may be brought to its highest state of oxidation.

An apparently necessary condition for the formation of the vanadium-cupferron precipitate seems to be a slight acidity of the solution. Experiments made in this connection showed that if aqueous solutions of sodium vanadate and of cupferron, both made neutral to litmus, were mixed the resulting solution became alkaline (evidently due to ammonia liberated), no precipitate being formed. This alkalinity must be overcome by addition of acid (hydrochloric or sulphuric) and a slight excess must be used in order to bring about complete precipitation.

The precipitate transferred to the filter is washed with a solution containing about 10 cc. of concentrated sulphuric acid and 1.5 grms. of cupferron per litre. The solutions and wash-liquid used should be cold; that is, their temperature should not exceed 20°C. If the temperature is allowed to rise much above this the precipitate tends to decompose and forms a gummy mass, which clogs the pores of the paper and makes filtering almost impossible. The precipitate is ready to filter about as soon as formed and there should be no delay in the filtration and washing. If

the precipitate is allowed to remain long on the filter it tends to crack and is then more difficultly washed, while if the process is carried out quickly and without interruption it is readily filtered and washed.

By this process the following results were obtained :—

TABLE III.

Exp.	Grms. NH_4VO_3 solution taken.	Grms. of V_2O_5 found.	Grms. of V_2O_5 per 25 grms. of solution.	
			Found.	Taken.
11.	25.4236	0.1686	0.1658	0.1655
12.	25.4193	0.1685	0.1657	0.1655
13.	25.3242	0.1673	0.1652	0.1655
14.	25.6816	0.1703	0.1658	0.1655

From the above data it appears that the vanadium in vanadates can be very accurately estimated by means of the cupferron reaction. Investigations are being made into the use of this reagent for the separation of vanadium from other elements, the results of which will appear at an early date.

Recently the statement has been made by Rodeja (*Abstract Journ. Am. Chem. Soc.*, 1915, ix., 2201; *Anales Soc. Espan. fis. quim.*, 1914, xii., 305, 379) that vanadium in the form of vanadates cannot be quantitatively precipitated by cupferron, but that if the vanadate is first reduced to the vanadyl condition a quantitative estimation of the vanadium may then be made. Experiments made according to the rather meagre details given in the abstract of this work failed to confirm this statement.

Four portions of a solution of sodium vanadate, two of which were precipitated without reduction and the other two after reduction, gave the following results :—

TABLE IV.

Exp.	Grms. of NH_4VO_4 solution taken.	Grms. of V_2O_5 found.	Grms. of V_2O_5 per 25 grms. of solution.
Without reduction.			
15	20.1067	0.0873	0.1085
16	20.4030	0.0882	0.1081
With reduction.			
17	54.1156	0.2300	0.1063
18	46.2709	0.1954	0.1056

The filtrate from Experiment 17 was evaporated and the residue ignited. A solution of this residue gave with cupferron a distinct test for vanadium.—*American Journal of Science*, xli., No. 244.

AZULENE, A BLUE HYDROCARBON.*

By ALFRED E. SHERNDAL.

(Concluded from p. 271).

THE work of Deussen and Philipp (*Ann.*, 1910, cclxxiv., 105), Semmler and Spornitz (*Ber.*, 1914, xlvii., 1029), and Semmler and Jakubowicz (*Ber.*, 1914, xlvii., 1141), on the sesquiterpenes of gurjun oil, gives interesting data for comparison with the dihydro-sesquiterpene from azulene. Deussen and Philipp found that oil of gurjun consists of two sesquiterpenes. Semmler and Jakubowicz then showed that these were both tricyclic, the crude oil, on reduction by hydrogen and platinum, absorbing only two hydrogen atoms, and yielding a dihydro product with sp. gr. at 20° 0.990; n_D 1.49; b. p. 115–117° at 7 mm. They succeeded further in separating the crude oil with the following characters :—Sp. gr. 0.922; O.R. –55°; n_D 1.507, into the two tricyclic sesquiterpenes :—

β -Gurjunene; sp. gr. 0.9348; O.R. +74.5°; n_D 1.50275.
 α -Gurjunene, sp. gr. 0.918; O.R. –95°.

The β -gurjunene, which forms about 33 per cent of the oil, resembles cedrene closely, but is not chemically

identical. It does not give the colour reactions characteristic of crude gurjun oil, and yields no blue oil on heating under pressure. Its reduction product by hydrogen and platinum has the characters :—

Sp. gr. 0.9258; n_D 1.49775; b. p. 120° at 8 mm.

α -Gurjunene gives the colour reaction of the crude oil, and on heating under pressure with air or oxygen yields a blue oil.

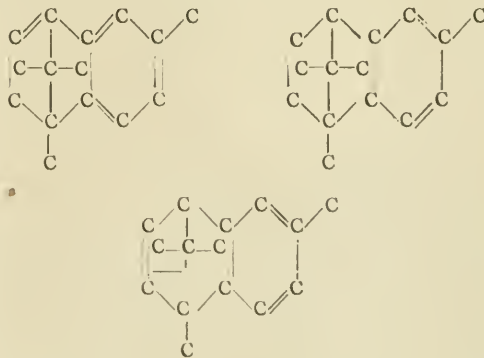
From these data the approximate constants of the dihydro- α -gurjunene can be derived :—Sp. gr. at 20° 0.900; n_D 1.492, which agree with those of the dihydro derivative from azulene. Summing up the characteristics of α -gurjunene we find :—(1) It gives the colour reactions characteristic of crude gurjun oil; (2) it yields azulene on heating under pressure with oxygen; (3) it is reduced to a tricyclic dihydro-sesquiterpene with constants and chemical behaviour such as colour reactions, similar to those of the reduction product from azulene. All these properties differ from those of other tricyclic sesquiterpenes such as β -gurjunene and cedrene. It is possible that other sesquiterpene types may be inverted by the reagents used, and so show some of the same properties.

It seems quite probable, however, that the α -gurjunene is the type which produces azulene, and that the dihydro-sesquiterpene formed by the complete reduction of azulene is identical with dihydro- α -gurjunene, although further experiments are necessary to demonstrate any such identity.

In the present state of our knowledge of the structure of the sesquiterpenes and the experimental data on azulene an attempt to ascribe a structural formula to the latter is necessarily purely speculative. Certain bases for a discussion of the possibilities are, however, not lacking; for instance :—

1. It is closely related to the sesquiterpenes in structure, as shown by the mode of formation and its reduction product.
2. It is tricyclic, and consequently contains four ethylene bonds.
3. It possesses an aromatic nucleus, indicated by the ready formation of a picrate.
4. It contains no hydroaromatic conjugate double bonds, since it is not reducible by sodium in alcohol.
5. It has a peculiar arrangement of the double bonds which accounts for its intense colour, such colour intensity being exhibited by no hitherto discovered hydrocarbon.

If we take, for the time being, the type formulæ suggested by Semmler, and consider the possibilities of oxidising to a tricyclic, tetra-, or pentocean molecule, $\text{C}_{15}\text{H}_{18}$, which could be reconciled with the above requirements, we arrive at structures such as the following :—



Whether or not the azulene molecule has some such structure can only be determined by further study, perhaps from its oxidation products. Its formation from the sesquiterpenes can aid but little in this direction, so long as their structure is so little known, but a synthesis from

* *Journal of the American Chemical Society*, xxxvii., No. 6.

substances of known structure does not seem impossible. In this connection the formation of the blue oil by the dry distillation of calcium adipate is interesting (Hentschel and Wislicenus, *Ann.*, 1893, cclxxv., 312). Such a synthesis would seem to give the greatest promise in indicating the structure of this remarkable substance, and would at the same time give additional evidence as to the structure of the sesquiterpenes to which it is related.

THE PRODUCTION OF SULPHURIC ACID AND A PROPOSED NEW METHOD OF MANUFACTURE.*

By WILLIAM H. WAGGAMAN,
Scientist in Fertiliser Investigations.

(Concluded from p. 274).

New Modification of the Chamber Process.†

THIS method is based on the fact that if a mixture of warm gases is drawn downward through a special flue their resistance to the downward pull, together with the constant change of their course, will tend to mix them very intimately, and unless the internal diameter of the flue is too great there will be practically no zones of inactivity in the apparatus. Moreover, the constant impinging of the gases on the walls of the spiral flue, which can be cooled either by air or water, makes it practicable to maintain the gases at a temperature most favourable for the efficient yield of sulphuric acid.

In the following laboratory experiments, however, the sulphur dioxide (SO_2) used was not directly derived from burning pyrites or sulphur, so it was necessary to heat the

The apparatus employed consisted, first, of a large test-tube, A, having a capacity of 200 cc. and containing a little water heated to boiling. The oxides of nitrogen, sulphur dioxide, air, and water vapour were led to the bottom of this vessel by separate tubes and given a preliminary mixing. From the test-tube the gases were drawn into the lead or glass spiral, B, which was heated to about 90°C . in order to facilitate the reactions. In winding downward through this spiral the warm gases were thoroughly mixed, with the result that most of the sulphuric acid produced in the system was formed in this coil. The residual gases were then passed through the absorption bulbs (D, D', D'') containing strong nitric acid, which absorbed the sulphur dioxide escaping oxidation in the spiral.

The quantities of sulphur dioxide converted into sulphuric acid in the tube A, and the spiral B, as well as that which escaped oxidation and was subsequently absorbed in the bulbs D, D', D'', were determined by analyses. The results of these analyses are given in Tables II. and III.

When the lead spiral was used (Table II.) the amount of sulphuric acid formed therein had to be determined by difference because of the formation of lead sulphate, which could not be entirely removed from the tube by washing.

On account of the many joints and rubber connections necessary in the apparatus there was some loss of sulphur dioxide in the system. When the lead spiral was used the amount of this loss could not be determined, so all the errors occurring in Table II. are thrown into column 5, making the figures for the sulphur dioxide oxidised in the lead spiral larger than they actually should be.

An inspection of Table II. shows that by passing sulphur dioxide, air, and water vapour through a lead spiral in the presence of an adequate supply of the oxides of nitrogen

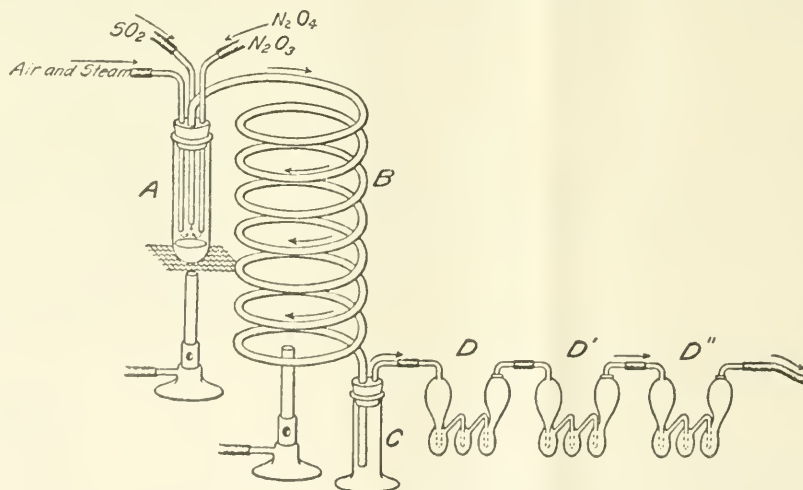


FIG. 1.—APPARATUS USED IN PROPOSED NEW METHOD FOR MANUFACTURE OF SULPHURIC ACID.

system artificially to attain a temperature as high as that obtained under factory conditions.

The sulphur dioxide was obtained from a small cylinder of the liquefied gas, which was weighed both before and after each experiment, and the SO_2 used thus determined. The oxides of nitrogen (chiefly N_2O_3 and N_2O_4) were produced by the action of dilute nitric acid on copper, and the rate at which they were used was roughly determined by allowing the gases to bubble through dilute sulphuric acid saturated with these gases. A mixture of air and water vapour was obtained by drawing air through a flask of water heated to the boiling-point.

the formation of sulphuric acid is practically complete, even when the gases are run at quite a rapid rate.

In ordinary chamber plants it is considered very good practice if only ten feet of chamber space is required for every lb. of sulphur burned in twenty-four hours. Figuring the chamber space required in run No. 8 it is seen that for every lb. of sulphur burned in twenty-four hours only 0.139 foot of chamber space was required.

While it is hardly fair to compare the results obtained in the laboratory with those obtained on a factory scale, still the efficiency of the apparatus can be more readily judged by expressing the results in the conventional way.

The well-known characteristic of some metals as well as metallic oxides and salts of acting as catalytic agents made it seem possible that the lead, lead oxide, or lead

* *Bulletin* 283, U. S. Department of Agriculture.

† Work carried on under the direction of Dr F. K. Cameron, to whom the author is indebted for much valuable assistance.

sulphate had something to do with the very efficient yield of acid obtained when using the lead spiral. Accordingly a glass coil of the same length and internal diameter was substituted in the experiments shown in Table III.

TABLE II.—Sulphur Dioxide oxidised to Sulphuric Acid in apparatus shown in Fig. 1. Lead Spiral used and steady stream of Oxides of Nitrogen furnished throughout experiments.

No. of run.	Time of run. Hours.	Rate per hour of SO ₂ . Grms.	SO ₂ oxidised in system.		SO ₂ lost in system. (a)	SO ₂ escaping from end of spiral. Per cent.
			In vessel A.	In lead spiral B.		
			Per cent.	Per cent.		
5	2	6.2017	32.07	67.92	—	0.1
7	2	6.4887	26.61	73.39	—	Trace.
8	2	7.6569	23.00	76.99	—	0.01

(a) Could not be determined. Included in the figures in column 5.

TABLE III.—Sulphur Dioxide oxidised to Sulphuric Acid in apparatus shown in Fig. 1. Glass spiral used and steady stream of Oxides of Nitrogen furnished.

No. of run.	Time of run. Hours.	Rate per hour of SO ₂ . Grms.	SO ₂ oxidised in system.		SO ₂ lost in system. (a)	SO ₂ escaping from end of spiral. Per cent.
			In vessel A.	In glass spiral B.		
			Per cent.	Per cent.		
20	1½	3.8311	14.17	75.14	3.15	7.34
19	1½	4.6404	43.99	50.18	3.20	2.63
12	2	5.7888	20.18	71.66	1.26	6.28

Table III. shows that the yield of acid was not so great with a glass as it was with a lead spiral. In no instance was the gas run through the apparatus so fast as in the experiments in Table II., yet even though the oxides of nitrogen were present in large quantities in the gaseous mixture there was a loss of sulphur dioxide from the end of the spiral.

In order to try out the catalytic action of the lead coil several runs were made with both the glass and lead spirals, but using no oxides of Nitrogen. The results of these experiments are shown in Tables IV. and V.

TABLE IV.—Sulphur Dioxide oxidised to Sulphuric Acid in apparatus shown in Fig. 1. Lead spiral used, but no oxides of Nitrogen employed.

No. of run.	Time of run. Hours.	Rate per hour of SO ₂ . Grms.	SO ₂ oxidised in system.		SO ₂ lost in system. (a)	SO ₂ escaping from end of spiral. Per cent.
			In vessel A.	In spiral B.		
			Per cent.	Per cent.		
21	1	3.2642	0.40	38.08	—	61.52
16	1	3.8459	0.41	40.78	—	58.81

(a) Could not be determined. Included in figures in column 5.

TABLE V.—Sulphur Dioxide oxidised to Sulphuric Acid in apparatus shown in Fig. 1. Glass spiral used, but no Oxides of Nitrogen employed.

18	10	2.6713	(a)	0.75	(b) 10.02	89.23
15	10	2.8393	0.40	0.68	(c) 12.36	86.56

(a) Included in next column.

(b) The large loss of sulphur dioxide in the system was due in part to the renewal of the sulphuric acid in the wash-bottle through which the gas was allowed to bubble before entering the system. This acid was not entirely saturated with SO₂ before these experiments were undertaken.

In comparing the results obtained in Tables IV. and V. it is evident that the lead spiral had some influence in the oxidation of the sulphur dioxide to sulphuric acid. The figures in column 5, Table IV., are obviously too high, since all the errors due to the loss of gas in the system are

thrown into this column; but while the sulphur dioxide and air was in each instance run through the lead spiral at greater speed than through the glass coil the quantity escaping oxidation was much less in the former than in the latter case.

In order to determine if the catalytic action observed in the lead coil was due to lead or lead sulphate two experiments were conducted using the glass spiral but no oxides of nitrogen. The conditions in these experiments were approximately the same as in those recorded in Table V. except that in the first run the interior of the glass coil was coated with precipitated lead sulphate and in the second a lead chain was introduced into the glass spiral. The results are shown in Table VI.

TABLE VI.—Sulphur Dioxide oxidised to Sulphuric Acid in glass spiral coated with lead sulphate and in the same spiral after the introduction of a lead chain.

No. of run.	Time of run. Hours.	Coil used.	Rate per hour of SO ₂ . Grms.	SO ₂ oxidised in system.		SO ₂ lost in system. P.c.	SO ₂ escaping from end of spiral. P.c.
				In vessel A.	In spiral B.		
				Per cent.	Per cent.		
22	1.0	(a)	2.6594	0.25	9.80	(b)	89.95
23	1.0	(b)	1.7523	0.09	53.60	(b)	46.31
24	1.5	(a)	2.5299	0.05	17.85	(b)	82.10

(a) Glass coil coated with lead sulphate.

(b) Not determined.

(c) Glass coil containing lead chain.

Here, again, as in Tables II. and IV., the amount of sulphur dioxide lost in the system could not be determined, but the results shown in Table VI. indicate that while lead sulphate has some influence on the oxidation of sulphur dioxide, lead or lead oxide is a much more energetic catalytic agent. The presence of the oxides of nitrogen in the system, however, is necessary for the complete oxidation of sulphur dioxide to sulphuric acid.

Factory Considerations.

In the construction of a sulphuric acid plant along the lines of the apparatus described in this paper it is proposed to dispense with the lead chambers and intermediate towers only. The lead spiral is not intended to replace the Glover Tower, which is so important in the preliminary mixing and cooling of the furnace gases and in restoring the oxides of nitrogen to the system, nor is it intended to do away with the Gay-Lussac tower, which is essential for the recovery of these same oxides of nitrogen from the residual gases.

The amount of lead required per cubic foot of chamber space is considerably greater for long spiral tube as herein suggested than for a cylindrical chamber in which the height and diameter are more nearly equal, but the great reduction in the chamber space required to produce sulphuric acid in the spiral should make it possible to build a plant with considerably less lead than is required in an ordinary chamber system. Moreover, the facts that the new type of plant requires no other device to accelerate the reactions and occupies much less ground space than the present type of factory, and therefore would not need large buildings, should decrease the initial cost of construction.

The cooling of the lead spiral would be accomplished largely by the air, but it necessary in hot weather streams of water could be played upon its upper portion. The water thus warmed by the heat of the reaction of the upper part of the spiral would tend to raise the temperature of the lower portion of the spiral where the reactions are not so vigorous. The immense amount of cooling surface contained in such a spiral, together with the constant movement of the acting gases, should also prevent excessive corrosion of the lead walls.

While it is not fair and hardly practicable to predict how efficient a plant built along the lines of the apparatus just described would prove, all the indications are that such

a scheme, worked on a factory scale, would be economically successful.

(NOTE.—Application has been made for a patent covering the process here described; if patent is allowed it will be donated to the people of the United States).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 1, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"*The Transmission of Electric Waves around the Earth's Surface.*" By Prof. H. M. MACDONALD, F.R.S.

A formula is obtained for the magnetic force at any point of the earth's surface supposed imperfectly conducting when the source is a simple oscillator normal to its surface. If $\eta = (\sigma/2\lambda V)^{1/2}$, where σ is the specific resistance of the earth at its surface, V is the velocity of radiation in the space outside the earth, λ is the wave-length of the oscillations, and $z = (2\pi a/\lambda)$, where a is the earth's radius, it appears that, when ηz is a small quantity, the effect of imperfect conduction is to increase the magnetic force at a distance from the oscillator, the ratio of the magnetic force in this case to the magnetic force when the conduction is perfect increasing with the distance from the oscillator and diminishing with increasing wave-length. When squares and higher powers of ηz are neglected, the results at angular distances from the oscillator of 6° , 9° , 12° , 15° , 18° for a wave-length of 5 kilometres agree with those derived from Love's results when the square of k/m is neglected. The effect of the terms involving squares of ηz is opposite to that of the first order terms. Values of the ratio are calculated from the general formula for wave-lengths of 5 kilometres and 2 kilometres, for a wave-length of 5 kilometres the ratio increases almost uniformly from 1.004 at an angular distance of 6° to 1.027 at 18° , and for a wave-length of 2 kilometres from 1.106 at 6° to 1.082 at 18° .

"*A Critical Study of Spectral Series. Part IV. The Structure of Spark Spectra.*" By Prof. W. H. HICKS, F.R.S.

The communication deals with the nature of the structure of spark spectra, using for this purpose the spectra of silver and gold. It is found that practically the whole of a spectrum in each case is built on a similar plan. Lines differ from other lines by constant differences of wave number called links, and sets of lines are connected by these links into chains or linkages attached each to one of the ordinary series lines. These links depend on successive Δ -displacements on the series limits where Δ is the displacement which gives the doublet separation, all of which may be calculated from data already known. The discussion is confined only to displacements on the β and s sequences. Those depending on the d sequences exist, but their discussion is postponed.

The links in question are—

$a = \beta - \beta(\Delta)$; $b = \beta(-\Delta) - \beta$; $c = \beta(-2\Delta) - \beta(-\Delta)$; $d = \beta(-3\Delta) - \beta(-2\Delta)$; $e = \beta(-3\Delta) - \beta(\Delta)$; $u = s - s(\Delta)$; $v = s(-\Delta) - s$. The long link e is due to a 2Δ displacement on each side of $\beta_2(1)$ or $VP_2(1)$, which on other grounds appears the more fundamental. These linkages are exhibited in the form of maps. From these when cleared of ambiguities formulæ for all the lines can be written down. These are given in tables for parts only of chains, as it is certain some of the links shown are only apparent and criteria for distinguishing the chance coincidences from real links are not wholly known.

"*On Periodic Disturbance of Level arising from the Load of Neighbouring Oceanic Tides.*" By K. TERAZAWA.

In Hecker's observations on the lunar deflection of gravity, the force apparently acting on the pendulum at Potsdam is a larger fraction of the moon's direct attraction when it acts towards east or west than when it acts towards north or south. A similar result has been found by Michelson in his observation of the lunar perturbation of water-level at Chicago. A calculation is here made to ascertain to what extent the tilting of the ground caused by the excess pressure of the tide in the North Atlantic is important for the explanation of this geodynamical discrepancy. Replacing the North Atlantic by a circular basin of radius 2000 km., taking the position of Chicago to be 1000 km. from the coast, and the rigidity of the earth to be 6×10^{11} c.g.s., it is found that the attraction effect of a uniform tide per metre of height is about 0.0024'', while its tilting effect is as much as 0.0069'', the maximum of the direct lunar attraction being 0.017''. If the surface of tide is ellipsoidal shelving towards the coast, nearly the same result is reached for the same mean tidal height.

"*Use of Partly Neutralised Mixtures of Acids as Hydron Regulators.*" By E. B. R. PRIDEAUX.

It has been shown that mixtures of acids have certain advantages over single acids which have been hitherto used for hydron regulators. The principle of inserting the acids required to make the neutralisation graph more nearly linear should be capable of wide application. A mixture of phosphoric, acetic, and boric acids has been investigated, the (H') values tabulated, and details given for the reproduction of these as standards. They were found to possess the advantages predicted.

"*Fossil Floras of the Coal Measures of South Staffordshire.*" By E. A. N. ARBER.

A flora of 58 species is described from a new horizon in South Staffordshire, the Red Clay Series or Old Hill Marls of Transition Coal Measure age. A new genus *Calamophloios* and a new species of *Sphenopteris* and *Cardiocarpus* are described, as well as several records new to this horizon.

Ten new records are added to the known flora of the Productive Series (Middle Coal Measures), including new species of *Calamites* and *Lepidostrobus*. A large number of additional records from new localities or horizons are added in respect of fossils already known from these beds.

NOTICES OF BOOKS.

Land for Fighting Men. Issued by the Incorporated English Beet Sugar Association, Liverpool.

THE Chairman of the Council of the English Beet Sugar Association, Mr. E. Russell Taylor, in this pamphlet makes the suggestion that the sugar beet could very profitably be grown in rotation by the settlers of the proposed experimental farming colonies for disabled soldiers and sailors. If the colonies were on a large enough scale, (in which case in Mr. Russell Taylor's opinion they would have to be about ten times as large as is proposed under the Government scheme), enough beet could be grown to supply a factory. The pamphlet lays fully justified stress upon the great value of the industry from the economic point of view, providing as it does employment for slack time, and benefiting auxiliary industries, while it has been shown to have a good effect upon the land and subsequent crops. The by-products are also of considerable value, and this opportunity of developing the new industry should certainly be seized.

Royal Society.—The Croonian Lecture, on "Evolution and Symmetry in the Order of the Sea-pens," will be delivered by Prof. S. J. HICKSON, F.R.S., on Thursday, June 22, at 4.30 p.m.

THE CHEMICAL NEWS

VOL. CXIII., No. 2952.

THE POSITION OF THE ABUNDANT ELEMENTS IN THE PERIODIC SYSTEM.

By JOHN WADDELL, B.Sc. (Lond.), D.Sc. (Edin.).

If we consider the groups of the elements as they are given in the periodic classification there seems to be a relationship that can scarcely be accidental between the atomic weights of the elements and the quantity in the earth's crust.

Lithium, though widespread, is small in quantity, sodium is far more plentiful, the amount of potassium too is considerable, while there is little rubidium and still less caesium. Similarly there is the gradation from little beryllium to much magnesium, less zinc, less cadmium, and again less mercury.

In the third group the same relationships hold between boron, aluminium, and gallium, while the higher members of the group are so rare that it is difficult to determine their order. In the fourth group silicon far exceeds carbon, titanium is much less abundant, and zirconium is rare.

Though there is much nitrogen in the atmosphere it is overbalanced by the phosphorus in the lithosphere, while arsenic, antimony, and bismuth are found in lessening quantities. Chlorine is more abundant than fluorine on the one hand and than bromine and iodine on the other, the last mentioned being least in quantity.

For the most part the elements in what is commonly called the typical series of the periodic table are most abundant, there being two exceptions, one unimportant, the other very conspicuous.

There are two members in the group of inert gases with lower atomic weight than argon, which is by far the most abundant of the group. Argon, however, might almost as logically be placed at the end of the typical series as at the beginning of the next. Oxygen, though in the series of less atomic weights than the typical series, is not only far more abundant than sulphur, which is in the same group of the typical elements, but nearly equals all other elements put together. Sulphur, selenium, and tellurium follow the general rule.

(Note.—After I had written the above I found that Prof. F. W. Clarke, in "The Data of Geochemistry," has given a number of the facts but in a somewhat different form, and he contents himself with the statement of fact).

There are various lines of argument that point to the existence of an element with an atomic weight between hydrogen and helium. It has been suggested that it is analogous to the halogens, but I am not aware of any argument for placing it in that group rather than with oxygen. If it belongs to the oxygen group it may well be much more active, the difference between it and oxygen being greater than between fluorine and chlorine. In this case its affinity may readily be conceived to be such that not only has it never been isolated but it has not even been suspected, and it is quite possible that compounds of this element with some other have been considered as elementary. This is not without precedent, for an oxide of vanadium was at first thought to be the element, and for a number of years the oxide UO_2 was considered to be the metal, and what is ordinarily called uranium nitrate is really the nitrate of this oxide. Now, as uranium, which is in Group VI., combines with oxygen in such a manner as to form a compound which was mistaken for an element, may it not be that what is called tellurium is really a compound of an element with an unknown element that may be called suboxygen or hyp-

oxygen? It is noticeable that the difference in atomic weight between antimony and tellurium is more than seven units, whereas the difference between arsenic and selenium is only about four units, and for the most part the difference in atomic weight between the members of the fifth and sixth groups is only one or two units.

We have, then, two facts to account for—first, the comparatively small quantity of elements of high atomic weight, and secondly, the small quantity of elements of the lowest atomic weight. With the exception of oxygen no element with an atomic weight less than sodium exists to the extent of 1 per cent, and if hydrogen is omitted all these elements put together do not reach 0.20 per cent, while sodium, magnesium, aluminium, and silicon combined amount to nearly 38 per cent.

It is almost impossible in this connection not to take into consideration the knowledge we have recently acquired regarding the three elements with the highest atomic weights—uranium, thorium, and radium. These are known to be disintegrating, uranium and thorium slowly, radium comparatively rapidly. Thorium and uranium were known for many years without there being the least suspicion that they were not perfectly stable, and the discovery of their disintegration may be considered almost accidental. We are able to detect their disintegration by its effect upon an electroscope for instance. Probably few of the elements except those only known by their radio-activity disintegrate in this way, but the disintegration may none the less exist. A number of elements were detected by the spectroscopy which might otherwise have continued to elude us; our only test for the existence of a still greater number is their radio-activity, and it is quite possible that with other means at our disposal we might be able on the one hand to discover new elements, or on the other hand to show that elements now regarded as stable are in reality unstable. In this case there would be a gradual disappearance of elements of high atomic weight, while the elements of low atomic weight would increase in quantity.

Why, then, do we have only a small quantity of the elements of lowest atomic weight? The answer seems natural—that the disintegration has not gone on long enough or far enough. There has so far not been much accumulation of the elements of lowest atomic weight. In some of the heavenly bodies the disintegration may have gone farther than on the earth. In the sun even the spectroscopy does not show the presence of uranium, or thorium, or radium, though helium, which is one product of disintegration of all these elements, is present. The gaseous stars give the spectrum of hydrogen and of helium, while few of the other elements are to be detected. It is generally considered that these are the hottest stars and that they are at an earlier stage of development than the sun. Some of the nebulae give lines in the spectrum unknown in the sun, which are attributed to an element to which the name nebulium has been given. The atomic weight of this element may be even lower than that of hydrogen.

If the gaseous stars and the nebulae are the result of disintegration of elements of high atomic weight they would belong to the late stages of development rather than to the early. Though this is different from the view usually held, is it not quite as reasonable that these hot gases are produced by the energy of disintegration as that matter on its first appearance should be at an exceedingly high temperature? So long as we knew of no sources of heat except those dependent on masses or molecules coming together, it was natural to conceive of the radiated heat being compensated by contraction of the body or by chemical action, but now that we have discovered that radium by disintegration produces several million times as much heat as the same weight of oxygen and hydrogen by their combination, the high temperature may be accounted for without the assumption that the gases were originally excessively hot.

Why is it that oxygen is in such large quantity? Again

we turn to the radio-active elements. These all seem to end with lead, so that there is lead derived from uranium and lead derived from thorium, as well as lead which appears to be without radio-active origin. All these different leads are alike in chemical properties and in spectrum, though there appears to be a difference in atomic weight. So it may be that oxygen is the end or the apparent end of the disintegration of a large number of elements, its change, if it does change, being very slow. The fact that, so far as we know, oxygen wherever obtained has the same atomic weight is a difficulty, but possibly not an insurmountable one. The process by which oxygen is produced from one element may be different from that by which it is produced from another, and the end product may be exactly the same instead of being, as in the case of radio-active elements, simply isotopic.

Queen's University, Kingston,
Canada.

A PECULIAR INTERGROWTH OF PHOSPHATE AND SILICATE MINERALS.*

By EDGAR T. WHERRY, National Museum, U.S.A.

A GREEN and white substance occurring associated with variscite in fissure veins in metamorphosed slate near Manhattan, Nevada, was recently submitted to the U.S. National Museum for identification by Mr. Percy Train of that place (U.S. National Museum Catalogue, No. 92,909). It appears to be of sufficient interest to justify this preliminary announcement of its character.

The material presents the form of a "sulphate" green glassy mass, traversed by numerous sub-parallel wavy white lamellæ, varying from 1 mm. down to 0.05 mm. in thickness, but at the latter size becoming too translucent to be distinguished, so that the variation may well continue to still thinner dimensions. Both minerals are practically amorphous, showing between crossed nicols only traces of weakly doubly refracting material.

A small sample of the purest green material which could be separated by hand-picking was submitted to J. E. Whitfield for analysis; it was free from visible lamellæ, although it may have contained indistinguishable ones. Its composition proved to be:—CaO, 6.30; CuO, 1.25; MgO, 0.80 (determined by the writer on a separate sample); Al₂O₃, 25.90; Fe₂O₃, 2.14; P₂O₅, 24.76; SiO₂, 7.32; H₂O below 100° 21.90, above 100° 9.20; sum, 99.57. These figures lead to no simple formula, but as it seemed probable that the silica might be due to lamellæ which are present but unrecognisable because of their thinness, an attempt was made to determine the composition of the white lamellar mineral. It proved impracticable to separate the lamellæ from a green ground-mass with any degree of completeness, but a very small sample, containing perhaps one-third of the latter, was analysed by the writer with the following results:—CaO + CuO, 9.0; MgO, 0.5; Al₂O₃ + Fe₂O₃, 23.3; P₂O₅, 12.1; SiO₂, 30.0; H₂O below 100°, 10.4; above 100°, 14.8; sum, 100.1.

Although amorphous colloidal minerals like these do not necessarily possess definite formulæ, it seemed worth while to attempt to determine at least their approximate nature. The known aluminium phosphate minerals fall into four divisions with reference to the ratios of the Al₂O₃ to P₂O₅, as shown in Table I.

The ratio Al₂O₃(+Fe₂O₃):P₂O₅ shown in Analysis 1 is 3.1:2, so that this mineral evidently belongs to the second of these divisions. It is also very high in water, and accordingly lies toward the bottom of the table. The pos-

sibility of its identity with vashegyite must therefore be considered. The latter mineral was described by Zimányi as a dense (*dicht, derb*) white meerschaum-like substance with the (rather improbable) ratios Al₂O₃:P₂O₅:H₂O = 4:3:30, associated with a similar material with the ratios 3:2:17 (*Math. Term. Ert.*, 1909, xxvii., 64; *Zeits. Kryst. Min.*, 1909, xlvii., 53). It seems likely that these are really the same mineral, the apparent difference in ratios being due to the impure character of the samples analysed. In Doelter's "Handbuch der Mineralchemie" (1914, iii., 465) this mineral is listed as amorphous, but a specimen labelled vashegyite in the collection of Colonel Roebing has been found by Dr. E. S. Larsen, jun., to be cryptocrystalline with an index of refraction of 1.480 and double refraction 0.002 (private communication). A comparison of the properties of the present mineral and vashegyite is given in Table II.

The differences in optical properties can be explained as due to the vashegyite examined by Dr. Larsen being a "metacolloid," a colloid exhibiting incipient crystallisation, while the Manhattan mineral is still essentially amorphous; the difference in colour is attributable to the presence of copper in the latter. (The copper probably replaces either some of the (AlOH)'' groups or H therein). The two minerals thus agree to a sufficient extent for them to be regarded as identical.

TABLE I.

Al ₂ O ₃ :P ₂ O ₅ ...	1:1.	3:2.	2:1.	3:1.
Formula ...	AlPO ₄ .	(AlOH)'' ₃ (PO ₄) ₂ '''.	(AlOH)''(AlO ₂ H ₂)'(PO ₄)'''.	(AlO ₂ H ₂) ₃ '(PO ₄)'''.
Excess H ₂ O:Al ₂ O ₃ .				
0:1	Berlinite.	Trolleite.	Angelite.	
1:1	Planerite.		Peganite.	Spherite.
2:1		Ceruleolac-tite (and turquois).		Some "rich-mondite."
3:1		Wavellite.	Fischerite.	
4:1	Callainite, lucinite and variscite.		Some "rich-Evansite. mondite."	
5:1		Vashegyite (two varieties).		
6:1	Some "rich-mondite" and zeph-arovichite.			

TABLE II.

	Manhattan mineral.	Vashegyite.
Colour	Pale green.	White to y lowish.
Lustre	Vitreous.	Dull.
Hardness	3.5.	2.5.
Specific gravity ..	1.98.	1.964.
Structure . . .	Amorphous, glass-like.	Compact meerschaum-like.
Optical character ..	Isotropic.	Anisotropic, cryptocrystal-line.
Index of refraction	Variable, 1.48 to 1.50	1.480
Double refraction ..	Absent.	Very weak, about 0.002.
Ratio— Al ₂ O ₃ :P ₂ O ₅ :H ₂ O	About 3:2:18.	3:2:17 or 4:3:30.
Impurities	Considerable, including copper oxide, yielding the green colour.	Very small in amount.
Occurrence	Associated with variscite.	"In the immediate neighbourhood of variscite."

* Published by permission of the Secretary of the Smithsonian Institution. From the *Journal of the Washington Academy of Sciences*, vi., No. 5.

The nature of the white lamellar mineral cannot be definitely made out from the data at hand. Of the constituents found in the second analysis, all of the P_2O_5 and part of the Al_2O_3 and H_2O are undoubtedly due to the admixed green material; if this amounted to one-third of the whole, then the approximate composition of the white mineral would be CaO 17, Al_2O_3 17, SiO_2 47, and H_2O 19, corresponding, roughly, to the ratios of these four constituents respectively, 2:1:5:7. No amorphous mineral of this composition appears to be on record, although the crystalline zeolite laubaniite differs only in having slightly less water. However, the mean index of laubaniite, as determined by Dr. Larsen is 1.475 (private communication), while that of the present mineral is higher, varying from 1.53 to 1.54, so the two must be entirely distinct. It may be noted that the mineral fuses with intumescence before the blowpipe, so that it evidently belongs to the zeolite group, but under the circumstances it would be unsafe to assign a name to it.

Although in many aluminium phosphates siliceous impurities have been found to be present, no definite intergrowth relations have heretofore been reported to exist between the two. The structure here shown is not difficult to explain, however, when the colloidal character of the materials is considered. The lamellæ have the aspect of forms produced by rhythmic precipitation in gels, such as obtained in many of the experiments described by Liesegang ("Geologische Diffusionen," Dresden and Leipzig, 1913) and others. In this case if, while the phosphate gel was still soft, a solution containing calcium and silica flowed over it, reaction might readily have occurred, with removal of part of the phosphoric acid and formation of a calcium aluminium silicate with the liberated alumina.

The material studied is regarded, then, as a colloidal vashegyite traversed by rhythmically precipitated laminae of a calcium aluminium silicate of probably zeolitic nature.

ON THE REACTION PRODUCTS OF SULPHUR DIOXIDE ON AMMONIA.

By MASATAKA OGAWA and SHINICHI AOYAMA.

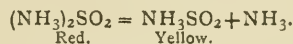
DÖBEREINER first mentioned that dry sulphur dioxide condenses with dry ammonia to a bright brown solid mass, which the smallest quantity of water converts into ammonium sulphite (Schw. Jahrb., xlvii., 120; Berz. J. B., 1826, vii., 151).

Rose worked much on this subject (Pogg. Ann., 1834, xxxiii., 235; 1837, xlii., 415; 1844, lxi., 397; Berz. J. B., xv., 167; xviii., 173; xxv., 262). In the earlier part of his work he described a crystalline substance of reddish yellow colour which is formed when the combination occurs in excess of ammonia and a more yellowish substance in excess of sulphur dioxide. He assumed the combination will occur in two different ratios: two volumes of ammonia to one volume of sulphur dioxide and one volume of ammonia to one volume of sulphur dioxide. But actually on starting from two volumes of ammonia and one volume of sulphur dioxide some of the ammonia was left uncombined, and on using excess of sulphur dioxide nearly equal volumes of the gases did combine. In the latter part of his work thus he modified the above statements by saying that the gases combine in equal volumes, producing one and the same single substance in whatever proportions the gases are taken. He called this substance "anhydrous ammonium sulphite." The aqueous solution, however, contained sulphate, trithionate, thiosulphate, and sulphite. So he thought this substance to be isomeric to the ordinary anhydrous ammonium sulphite.

Forchhammer (Comptes Rendus, v., 395) found that besides the yellow substance a white substance is produced by the combination of the two gases in the dry state. According to him the white substance is hydrated

ammonium sulphate and the coloured substance an amide of sulphur.

Schumann got a yellow substance by the action of dry ammonia on excess of sulphur dioxide, the both gases being cooled at about 0° (Zeit. Anorg. Chem., 1900, xxiii., 49). The analytical result was closely concordant with the formula NH_3SO_2 . He got also another substance of red colour, having the composition $(NH_3)_2SO_2$. This was obtained by the interaction of the gases in excess of ammonia, keeping the vessel in which the reaction occurs at a temperature from -5° to -7° . On warming the red substance ammonia was given off, leaving a yellow substance quite similar to that obtained by the interaction of the gases in excess of sulphur dioxide, and expressed the change according to the simple equation—



Without knowing Schumann's work Divers and one of us published a paper entitled "Ammonium Amidosulphite" almost at the same time (Journ. Chem. Soc., 1900, lxxvii., 327). According to them dry ammonia and dry sulphur dioxide condense to a white substance in presence of excess of the former, when dry ether is made use of and the reaction flask is kept well cooled, being immersed in a bath of ice and salt. The white substance was expressed as ammonium amidosulphite $NH_2SO_2NH_4$ or $(NH_3)_2SO_2$.

The white substance soon decomposes on a slight warming, giving off ammonia, and leaves a residue coloured orange, which is a mixture of several substances, among which ammonium imidosulphite $NH(SO_2NH_4)_2$, sulphamide $(NH_2)_2SO_2$, &c., can be found.

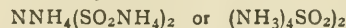
Ephraim and Piotrowski (Ber., 1911, 379) tried the action of thionyl chloride on liquid ammonia and got an intense red coloured substance, which is very similar in appearance to the product obtained by Schumann, by the action of sulphur dioxide on excess of ammonia. On treating the red substance with a solution of ammoniacal silver nitrate a silver salt of the composition $NaAg(SO_2Ag)_2$ was obtained as a purple-red substance. From the result they concluded the first formed red substance was disulphinamide—



and the imidosulphite $NaAg(SO_2Ag)_2$ was formed as the result of the subsequent hydrolysis of disulphinamide, according to the equation—



They raised an objection against Schumann as regards the red substance being ammonium amidosulphite $NH_2SO_2NH_4$ or $(NH_3)_2SO_2$, for it is highly improbable that while the free acid NH_2SO_2H or NH_3SO_2 itself being only pale yellow coloured, the ammonium derivative of ammonium imidosulphite—



be so intense coloured and not $(NH_3)_2SO_2$. They add also that derivatives of which imido or amido hydrogen is replaced by metals are all coloured, so it is rational that the Schumann's substance has a red colour if the formula $NNH_4(SO_2NH_4)_2$ is adopted. At the same time they opposed Divers and Ogawa, denying the existence of ammonium amidosulphite as a white substance and the orange coloured substance as the product of the decomposition on the ground that even in the temperature of boiling liquid ammonia, -38° , the red coloured substance was obtained by them while the white undecomposed salt was got by Divers and Ogawa only at a temperature of a mixture of ice and salt.

So far the knowledge of the reaction is still imperfect, especially in connection with the question whether ammonium amidosulphite is a white substance (Divers and Ogawa), or the red substance (Schumann), or the substance is not ammonium amidosulphite but really is triammonium imidosulphite (Ephraim and Piotrowski). Our present investigation is attempted to give some light on

these points and also to ascertain the nature of the compound $N_4H_{12}S_5O_{10}$, which Divers and Ogawa have left in an incomplete state.

Sulphur Dioxide and Excess of Ammonia.

On repeating the experiment done by Schumann we got an orange coloured mass whose composition was not definite, but the atomic ratio of nitrogen to sulphur found was always far less than 2 : 1. As a very large quantity of heat is produced when the combination occurs, the ratio of sending of the gases has an important factor on the composition of the product.

On using ether and following closely the direction given by Divers and Ogawa we got a perfectly white substance formed in the inside of the reaction flask, immersed in the bath of ice and salt, but in the inside of the neck of the flask, which is in the outside of the flask, an orange coloured substance was seen to be produced. After decanting the ammoniacal ether off and removing the adhered ether by passing a current of dry ammonia for some hours the dry white substance remained without change for some time, even brought to the room temperature (about 14°) if kept in an atmosphere of ammonia. The whole operation of drying the salt was carried on in the freezing mixture. The results were exactly the same as observed by one of us thirteen years ago. There is no more doubt of the formation of the compound $NH_2SO_2NH_4$ as a white substance.

In order to ascertain what is formed by the decomposition of the amidosulphite at the room temperature the following experiments were performed. By passing a current of dry hydrogen over the white substance in the flask at the temperature of the room (16°) ammonia escaped and at the same time the colour changed from yellow to orange. As the passage of the hydrogen continued evolution of ammonia slackened more and more but never ceased even after three days of the continued process. So it was evident that the product should vary in composition. However, we analysed the product after the evolution of ammonia became so very much smaller that we thought it might be neglected. So we found that the composition varies from $(NH_3)_4(SO_2)_3$ to $(NH_3)_{10}(SO_2)_9$. We expected we should get the substance having the composition NH_3SO_2 if we were patient enough to drive away ammonia. But the product obtained each time was evidently heterogeneous, consisting of differently shaded mass, with yellow to red. Thus we gave the experiment up, knowing the product was not a definite compound.

The freshly prepared white salt when dissolved by ice-cold water gave a solution answering all the tests for pure ammonium sulphite, while the coloured mass when dissolved by ice-cold water furnished a solution indicating the presence of sulphite, sulphate, trithionate, and sulphamide.

Ammonia and Sulphur Dioxide in Excess.

The experiment was carried in a similar way as in the case of the above experiments, only difference being that sulphur dioxide was kept in excess during the preparation. The reaction product was a pale yellow powder. On warming slightly it evolved sulphur dioxide and became an orange coloured mass apparently same as that obtained from the white salt. To remove the ether adhered to the yellow substance we passed a current of sulphur dioxide while the preparation flask was immersed in ice-cold water. But we did not succeed in removing all the ether in this way. If the preparation flask was taken out from the ice water and kept at the room temperature the yellow mass became spontaneously orange, indicating decomposition.

So we analysed the substance while still moistened with ether.

Analysis.—The salt was dissolved in cold water and distilled with potash. The evolved ammonia was received in a standard hydrochloric acid and the remaining acid was titrated back with a standard alkali solution. The residue

remaining in the distillation flask was oxidised with bromine and after acidification with hydrochloric acid barium sulphate was precipitated and weighed.

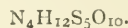
The calculated and found percentages are :—

			Ammonia.	Sulphur dioxide.
NH_3SO_2	..	Cal.	21.03	—
"	..	Found	21.83 (18.41)	78.97
"	..	"	21.01 (20.61)	78.09 (65.90)
				78.99 (77.36)

(Figures in parentheses are percentages in the stuff still moistened with ether, and those preceding them are recalculated percentages from the former, on the assumption that the salt is a compound of ammonia and sulphur dioxide).

It will be seen that the analysis establishes the composition of the salt to be NH_3SO_2 . The constitution may be probably NH_2SO_2H .

Properties.—It is a powdery substance of pale yellow colour. Warmed very slightly it soon begins to decompose to orange coloured substances. The aqueous solution of the salt reacts acid and contains sulphite, sulphate, trithionate, and sulphamide, just the same as the solution obtained from partially decomposed ammonium amidosulphite—



The compound was obtained as crystals in the form of short thick prisms almost cubical in appearance by Divers and one of us (*Journ. Chem. Soc.*, 1901, lxxix., 1102) on treating the orange mass of decomposed ammonium amidosulphite with 95 per cent alcohol and on evaporation in desiccator. The crystals are neutral and have a bitter taste, not a sulphurous one; they are freely soluble in water and very deliquescent. The solution is unstable, the fresh solution gives no barium salt precipitate, even in presence of ammonia. Also it does not decolorise iodine solution and only slowly decolorises cold acid permanganate. It does not give the ferric chloride coloration of a thiosulphate. The solution becomes very acid after a time and then smells of sulphur dioxide.

The above is about all in relation to the properties of the compound given by Divers and Ogawa. About the constitution nothing is known. Since then, as no one has touched the subject, we have resumed it.

Ammonium amidosulphite was decomposed by heating at a temperature from 30 to 35° , and the orange mass thus obtained was digested with absolute alcohol. A beautiful red solution was thus obtained. After decanting off the red solution a fresh quantity of absolute alcohol was added and the extraction was repeated until no more red colour passed into the alcohol. The extraction then was done by 95 per cent alcohol, to which a yellow colour passed.

Both absolute alcohol and 95 per cent alcohol extracts were put separately in the desiccator. After much alcohol had been evaporated away apparently cubical crystals began to appear in both vessels. The mother liquor of absolute alcohol extract remained a deep red colour while the mother liquor from 95 per cent alcohol extract became yellow. The red mother liquor soon became yellow on exposure to a moist air. The crystals were purified on recrystallisation from ammoniacal alcohol. On analysing the crystals the following results were obtained :—

Ogawa and Aoyama.

		1.	2.	3.
Nitrogen (per cent) ..		12.93	12.65	12.18
Sulphur ..		42.25	41.18	41.74

Divers and Ogawa.

		1.	2.	3.	4.	5.
Nitrogen (p.c.) ..		14.43	14.11	14.36	14.02	14.40
Sulphur ..		41.24	41.14	40.82	41.02	—

On comparing the results with those obtained by Divers and Ogawa figures of nitrogen are all considerably low. The crystals of our preparation agreed with those of Divers

and Ogawa in all properties except being not very deliquescent. When the crystals were dissolved in aqueous alcohol and stood in the desiccator for a long time the re-formed crystals were found mixed with needle-shaped crystals. Supposing the latter crystals might be formed by the action of water on the former we diligently collected the needle-shaped crystals on repeated treatment of the cubical crystals with aqueous alcohol and analysed. The analytical result was nearly concordant with ammonium tetrathionate, as is shown below:—

	Nitrogen.	Sulphur.
$(\text{NH}_4)_2\text{S}_4\text{O}_6$	10.78	49.25
$(\text{NH}_4)_2\text{S}_4\text{O}_6 \cdot \text{H}_2\text{O}$..	10.44	46.06
Found	10.32	47.27

Qualitative Reactions.—A white precipitate is formed on addition of stannous chloride. No precipitate is formed by barium chloride, no precipitate is formed on addition of ammoniacal silver nitrate, no precipitate is formed on boiling with copper sulphate; no coloration is produced with ferric chloride; a black precipitate is formed with mercurous nitrate.

All these reactions are those of a tetrathionate.

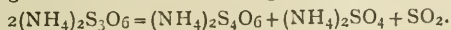
Effect of Heating the Salt.—The dry salt was introduced in a tube and heated in a current of nitrogen, using a bath of sulphuric acid. The decomposition began at about 130° ; sulphur dioxide was given off and a part of sulphur sublimed, while ammonium sulphate was left behind in the tube mixed with some sulphur. The sulphur dioxide evolved was absorbed in a solution of caustic potash and oxidised with bromine followed by hydrochloric acid. The sublimed sulphur as well as the sulphur mixed with ammonium sulphate were separated on dissolving away the ammonium sulphate with water and oxidised with a fuming nitric acid, and finally was precipitated as barium sulphate. Lastly the aqueous solution of the sulphate was also precipitated with barium chloride:—

	Found.	Calculated.
Sulphur dioxide sulphur ..	11.92	12.30
Free	24.03	24.62
Sulphate	11.96	12.30

The calculation was done using the following equation, $(\text{NH}_4)_2\text{S}_4\text{O}_6 = (\text{NH}_4)_2\text{SO}_4 + \text{SO}_2 + 2\text{S}$.

That ammonium tetrathionate will decompose on heating in this way has hitherto not been proved experimentally, yet Divers and Ogawa already inferred from analogy of the decomposition of ammonium trithionate, $(\text{NH}_4)_2\text{S}_3\text{O}_6 = (\text{NH}_4)_2\text{SO}_4 + \text{SO}_2 + \text{S}$.

From the above experiments it becomes now quite evident that the substance appearing in the form of silky needles is ammonium tetrathionate. The mother substance may certainly be ammonium trithionate, producing the tetrathionate according to the equation—



The deduction was further confirmed by the analysis of the cubical crystals as follows:—

	Nitrogen (per cent).	Sulphur (per cent).
$(\text{NH}_4)_2\text{S}_3\text{O}_6$	12.30	42.13
Found	12.56	42.18

Conclusions.

By the union of sulphur dioxide with ammonia there result two distinct substances. One is amidosulphurous acid, $\text{NH}_2\text{SO}_2\text{H}$, and the other is its ammonium salt, $\text{NH}_2\text{SO}_2\text{NH}_4$. The former is coloured pale yellow and the latter white.

The orange or red coloured substance is only formed as the result of the decomposition of the ammonium amidosulphite or amidosulphurous acid. We cannot agree with the reasoning of Ephraim and Piotrowski that the coloured substance is not decomposition product (*ante*). Even at the temperature of boiling liquid ammonia the heat pro-

duced by the reaction will be sufficient to cause the decomposition if proper care is not taken to regulate the current of the reacting gases and to diffuse the heat.

The compound $\text{N}_4\text{H}_{12}\text{S}_5\text{O}_{10}$ does not exist. The body obtained by Divers and Ogawa is impure ammonium trithionate.—*Science Reports, Tohoku Imperial University, Japan*, ii., No. 3.

HEXABROMODIACETYL.*

By C. LORING JACKSON and ROGER ADAMS.

IN an earlier paper (*Am. Chem. Journ.*, 1913, i., 341) A. H. Fiske and one of us described two acids, one melting at 207° , the other at 174° , made by the action of sodium hydroxide on tetrabromo-*o*-quinone, and it was also stated that, when treated with bromine and water, these acids were converted into a yellow diketone, to which the formula $\text{CBR}_3\text{CHBrCOCOCBR}_3$ was assigned. On continuing the study of this compound we have found that this formula is not the true one, but that it is really the hexabromodiacetyl $\text{CBR}_3\text{COCOCBR}_3$. The data on which this conclusion rests are given in Table I. containing all the analytical results obtained by us from the substance itself and its principal derivatives. The first column gives the percentages calculated for $\text{CBR}_3\text{CHBrCOCOCBR}_3$, the second the data obtained by Dr. Fiske in the earlier part of the work, the third those obtained in the work described in this paper, and the fourth the percentages calculated for $\text{CBR}_3\text{COCOCBR}_3$.

This table brings to light the astonishing fact that the percentages calculated for the two formulae of the diketone and its methyl and ethyl hemiacetals differ by less than 1 per cent, so that it is impossible to distinguish between them by these analyses, and, further, that the data at hand, when the earlier paper was written, justified the adoption of the heptabromomethyldiacetyl formula instead of that of the hexabromodiacetyl, since the results from the benzyl compound, which alone told against it, remained unintelligible until our later work had shown the ease with which bromine is replaced by hydrogen in these substances.

When at last the nature of this benzyl derivative was understood, it became one of our strong arguments in favour of the hexabromodiacetyl formula, which was established without question by the molecular weight determinations, the analyses of the other reduction products, and especially by the fact that the compound formed from it by the action of acetone was identical with tetrabromodiacetyl made from bromine and diacetyl in its melting-point $94-95^\circ$ (uncorr.), and in its very characteristic yellow coffin-shaped crystals. The heptabromomethyldiacetyl and its derivatives therefore must be struck from the list of known compounds.

So far as we can find, hexabromodiacetyl has been prepared only from tetrabromo-*o*-quinone as described in this paper. Some attempts of our own to prepare it with bromine and diacetyl led only to the known tetrabromodiacetyl in confirmation of the work of our predecessor (Keller, *Ber.*, 1890, xxiii., 35), and when we tried to introduce more bromine into this substance by exposing a mixture of it with bromine to the sunlight, no action was observed. Upon heating the mixture in a sealed tube an action took place, but the product was so tarry that we did not continue our experiments in this direction.

The most striking property of the hexabromodiacetyl is the ease with which it forms the monomethylhemiacetal, $\text{CBR}_3\text{COC}(\text{OHOCH}_3)\text{CBR}_3$, melting at 105° (uncorr.), or the corresponding ethyl compound melting at $96-97^\circ$ (uncorr.) by standing in the cold with the alcohol (*Am. Chem. Journ.*, 1913, i., 367).

(NOTE.—The melting-points in this earlier paper are

* *Journal of the American Chemical Society*, xxxvii., No. 11.

TABLE I.

	1. CBr ₃ CHBrCOCOCBr ₃ .	2. Fiske.	3. Adams.	4. CBr ₃ COCOCBr ₃ .
Br	85.90	85.78, 86.00	85.88	85.70
C	9.20	9.84, 9.47	8.62	8.57
H	0.15	0.58, 0.50	0.40	0.0
MW	653	—	514, 512 (a)	560
<i>Methyl Alcohol Addition.</i>				
	CBr ₃ CHBrCOC(OHOC ₂ H ₅)CBr ₃ .			CBr ₃ COC(OHOC ₂ H ₅)CBr ₃ .
Br	81.75	81.21, 81.32	81.17, 81.01, 81.27 (b)	81.08
C	10.51	10.52	10.26	10.14
H	0.73	0.97	0.86	0.68
MW	685	—	584, 588, 601 (c)	592
<i>Ethyl Alcohol Addition.</i>				
	CBr ₃ CHBrCOC(OHOC ₂ H ₅)CBr ₃ .			CBr ₃ COC(OHOC ₂ H ₅)CBr ₃ .
Br	80.11	80.17, 79.75	79.30, 79.11 (c), 79.52	79.20
C	12.01	12.35	12.01, 11.99	11.88
H	1.00	1.25	1.12, 1.09	0.99
MW	699	—	597, 582	606
<i>Benzyl Alcohol Derivative.</i>				
	CHBr ₂ CHBrCOC(OHOC ₇ H ₇)CBr ₃ .			CHBr ₂ COC(OHOC ₇ H ₇)CBr ₃ .
Br	70.48	67.89, 68.29	68.01 (d)	67.92
C	21.12	22.58	22.43	22.42
H	1.32	1.90	1.77	1.53
MW	681	—	580, 575, 577	589
<i>Acetone Reductions.</i>				
	CHBr ₂ CHBrCOCOCCHBr ₂ .			CHBr ₂ COCOCCHBr ₂ .
Br	80.81	—	79.68, 79.80, 79.58 (e)	79.60
MW	495	—	375, 383	402
	CHBr ₂ CHBrCOC(OHOC ₃ H ₇)CBr ₃ .			CHBr ₂ COC(OHOC ₃ H ₇)CBr ₃ .
Br	77.41	—	76.02, 76.43 (f)	75.91
C	13.55	—	13.86	13.67
H	1.29	—	1.54	1.32
MW	620	—	502	527

(a) Subs. 0.7705, 1.3457, Δ 0.57, 1.0, C₆H₆ 12.874. Subs. 0.3010, 0.2348, AgBr 0.6074, CO₂ 0.0742, H₂O 0.084.
 (b) Subs. 0.1483, 0.1987, 0.2394, 0.3090, AgBr 0.2829, 0.3783, 0.4571, CO₂ 0.1162, H₂O 0.0241. Subs. 0.2151, 0.4482, 0.6655, Δ 0.15, 0.31, 0.45, C₆H₆ 12.290.
 (c) Subs. 0.1515, 0.1449, 0.1210, 0.2324, 0.2523, 0.2256, 0.5057, AgBr 0.2823, 0.2693, 0.2261, CO₂ 0.1024, 0.1110, H₂O 0.0235, 0.0248, Δ 0.15, 0.345, C₆H₆ 12.580.
 (d) Subs. 0.1602, 0.2457, 0.2292, 0.4267, 0.7335, AgBr 0.2560, CO₂ 0.2021, H₂O 0.0393, Δ 0.165, 0.31, 0.53, C₆H₆ 11.971.
 (e) Subs. 0.1918, 0.1529, 0.1271, 0.2465, 0.6717, AgBr 0.3591, 0.2866, 0.2381, Δ 0.27, 0.72, C₆H₆ 12.164.
 (f) Subs. 0.1427, 0.1416, 0.2230, 0.1850, AgBr 0.2549, 0.2543, CO₂ 0.1133, H₂O 0.0309, Δ 0.135, C₆H₆ 13.639.

somewhat lower than those given above, which is principally due to our discovery that petroleum ether is an almost perfect solvent for these compounds).

So far as we know, these are the first hemiacetals prepared from diketones with open chains, but such compounds have been obtained from ring diketones and the closely related para and orthoquinones (Zincke, *Ann.*, cclxvii., 319, 331; Jackson, Grindley, *Am. Chem. Journ.*, 1895, xviii., 579; Jackson, MacLaurin, *Ibid.*, 1907, xxxviii., 127; Jackson, Flint, *Ibid.*, 1908, xxxix., 80). This easy formation of hemiacetals from hexabromodiacyetyl, CBr₃COCOCBr₃, seemed to us to deserve study, but we have had time to try only a few experiments, and therefore all the statements which follow are liable to revision after a fuller study of this subject. It seems probable that the diketone structure is more favourable to the formation of hemiacetals than the ketone, since we were unable to make one by the action of alcohol on pentabromoacetone; but in spite of this the diketones apparently stand at the bottom of the list of hemiacetal producing compounds, since it was necessary to have this structure reinforced by the six atoms of bromine, neither tetrabromodiacyetyl, nor dibromodiacyetyl, nor diacyetyl itself showing any trace of the formation of a hemiacetal, when treated with alcohol. Aldehydes and quinones, on the other hand, need much less help from the presence of

halogens, the monochloroaldehyde certainly forming a hemiacetal, and it is even possible that aldehyde itself does, although the evidence in this case is not convincing (Jacobsen, *Ber.*, 1871, iv., 215; Renard, *Ibid.*, 1875, viii., 132). Tetraethoxy-*p*-quinone also forms an unstable hemiacetal, although in this case by the action of sodium alcoholate instead of alcohol, and both the para and orthoquinones give stable hemiacetals with much less halogen (two to three atoms) than the diketone.

The hemiacetals derived from hexabromodiacyetyl show a remarkable stability toward acids. In fact, we have not succeeded in recovering the diacyetyl from them, whereas chloral alcoholate is decomposed by strong sulphuric acid in the cold, and the hemiacetals of the paraquinones even by dilute hydrochloric acid at ordinary temperatures, while those of the orthoquinones, although more stable, yield to acids at higher temperatures. It is interesting that in these cases the greater stability belongs to substances with the carbonyls adjacent. In view of the easy formation of hydrates from substituted aldehydes it is strange that we have observed no sign of the formation of a hydrate from hexabromodiacyetyl.

In all the hemiacetals isolated by us only one of the carbonyls of the hexabromodiacyetyl was affected by the alcohol, but there are some indications that the action could extend to the other also, since, when the diketone

stood for a long time with absolute methyl alcohol, a thick red oil was obtained instead of the crystalline hemiacetal, and, when it was boiled with alcohol, a less pure product resulted than in the cold. Both of these observations can be explained by the formation of a dihemiacetal, but more experiments are necessary before this explanation is accepted. The orthoquinones show a similar tendency to form monohemiacetals.

We consider these compounds hemiacetals, because we can find no other way in which the alcohol could be attached to the diketone, and this view is supported by the formation of an oxalic ester in addition to bromoform (*Am. Chem. Journ.*, 1913, 1., 368) when the ethyl compound was decomposed with water at 100°. Some of their properties, however, are different from those we should have expected of hemiacetals. For instance, their stability toward acids, since they were not decomposed by boiling hydrobromic acid, or by dilute sulphuric acid boiling at 135°. At 150° the acid decomposed them, but no hexabromodiacyl was recovered. Further, acetic anhydride or acetyl chloride had no action on them in spite of the hydroxyl they contain. Although these properties are unexpected they are not incompatible with the hemiacetal formula. These hemiacetals are somewhat more stable toward alkalis than the hexabromodiacyl, but are decomposed by them with the formation of bromoform, and at least in the ethyl compound an oxalic ester. A greater stability is also shown by the fact that they are unaffected by hydriodic acid, which acts on the mother substance in a way to be described presently.

The hexabromodiacylmonomethylhemiacetal was observed in three different sorts of crystals when the solvent used was petroleum ether. (a) Long needles; (b) short broad square ended prisms, which may have been only a different habit of the first form; and (c) octahedra apparently of the tetragonal system, whereas the other two seemed to be orthorhombic. This last form also has a much more brilliant lustre than the others. All three melted at 105° (uncorr.), and could be converted into the first form by recrystallisation. On the other hand, the ethylhemiacetal was observed only in long narrow plates.

Benzyl alcohol acted on the hexabromodiacyl in a more complex way than the fat alcohols, giving a compound containing only 5 atoms of bromine, for which we have worked out two constitutional formulæ, either pentabromodiacylmonobenzylhemiacetal, $\text{CHBr}_2\text{COC}(\text{OHOC}_6\text{H}_5)\text{CBr}_3$, or benzoyloxy-pentabromodiacyl, $\text{C}_7\text{H}_5\text{OOCBr}_2\text{COCOCBr}_3$. We give the preference to the first of these formulæ for the following reasons:—The percentages of hydrogen found agree very well with this formula, but differ from that required by the second by a greater amount than is found in any other work by the two analysts who made them. The formation of a hemiacetal is characteristic of the behaviour of the other alcohols with hexabromodiacyl, whereas no other alkyloxy compounds have been observed. Hexabromodiacyl undergoes the replacement of bromine by hydrogen also with acetone or hydriodic acid. The substance is more stable toward alkalis than the mother substance; this property is shown by other hemiacetals, whereas a substance with the second formula would probably be less stable. Alkalis give no bromoform with it.

Metanitrobenzyl alcohol did not combine with hexabromodiacyl.

A few attempts to reduce the carbonyls in hexabromodiacyl gave unsatisfactory results, but hydriodic acid converted it into tetrabromodiacyl by replacing two atoms of bromine by hydrogen, and the same product was obtained more easily with acetone in the cold. If alcohol was mixed with the acetone the product contained pentabromodiacylmonomethylhemiacetal, $\text{CHBr}_2\text{COC}(\text{OHOC}_2\text{H}_5)\text{CBr}_3$, melting at 115° (uncorr.); but acetone mixed with methyl alcohol gave no replacement of bromine by hydrogen, the only product being hexabromodiacylmonomethylhemiacetal.

In forming the pentabromohemiacetals the replacement of bromine by hydrogen would be likely to take place in

the CBr_3 next the unaltered carbonyl, if it happened after the formation of the hemiacetal (which is by no means established), and this view is supported by the observation that no bromoform could be detected when the ethyl or benzyl pentabromo compound was decomposed by an alkali, whereas the hexabromohemiacetals give bromoform under these conditions. We have therefore formulated these compounds accordingly.

When hexabromodiacyl was treated with an aqueous solution of potassium iodide, iodine and carbonic dioxide were set free, and a new compound obtained, which melted with decomposition at 120–125°. We think that this substance is the triiodobromoacetone, $\text{Cl}_3\text{COCH}_2\text{Br}$, but cannot support this opinion by conclusive evidence. The discussion of this subject will be found in the Experimental Part.

The substance melting at 71–72° mentioned in the previous paper (Jackson, Fiske, *Am. Chem. Journ.*, 1913, 1., 366) as formed by the action of water on the hexabromodiacyl, and also as a secondary product in its preparation, has been recognised as pentabromoacetone. It was also obtained by the action of perhydrol or constant boiling hydrobromic acid at 100° on the hexabromodiacyl. We are unable to understand the mechanism of these reactions, but they are not without analogy, as pentabromoacetone is also formed by the action of hydrogen dioxide on tetrabromodiacyl (Keller, Maas, *Centralb.*, 1898, i., 24).

(To be continued).

INTERNATIONAL INSTITUTE OF AGRICULTURE.

THE May issue of the *Bulletin of Agricultural and Commercial Statistics*, published by the International Institute of Agriculture, contains information as to the areas sown and the condition of crops in the Northern Hemisphere.

Dealing with the areas under cereal crops, amongst the most important of the new data incorporated in the present *Bulletin* are those of Italy (Wheat 4,760,000 hectares, or 94.1 per cent of last year's area and 100.3 per cent of the average of the five years' period 1909 to 1913; rye 120,000 hectares, or 100.8 and 97.9 per cent of that of last season and of the five years' average respectively; barley 246,000 hectares, or 100 per cent and 99.2 per cent respectively; oats 500,000 hectares, equivalent to 102.3 per cent and 98.6 per cent), and of Sweden (winter wheat with 115,439 hectares, or 122.2 per cent of the average of 1909 to 1913, and winter rye with 372,730 hectares, or 94.9 per cent of that average. The data previously published by the United States as regards area under winter wheat have been modified and are now given as 13,362,864 hectares, or 78.6 per cent of last season's and 116.4 per cent of the average 1909 to 1913).

Slight corrections have been made in the figures of area under wheat in British India, and the forecast of yield in that country is as follows:—86,262,390 quintals, or 82.5 per cent of that estimated for last season and 90.1 per cent of the five years' average 1909 to 1913.

The condition of the winter crops is generally satisfactory in France, although the unfavourable weather has hindered field work and delayed spring sowings.

Winter crops are also in fairly good condition in Great Britain and Ireland, in Italy, the Netherlands, and Switzerland, and moderately satisfactory according to the latest advices from the United States.

Winter crops suffered a good deal in Hungary from the wet season, and though the earlier seedings are well developed, those of a later date were prejudiced by the cold.

Plentiful snow in the month of March served to protect the winter crops in Canada, so that any winter killing has not been of importance.

The wheat crop promises well in Tunis, and the proximity of locust swarms has caused very little anxiety.

The *Bulletin* also affords information on the state of the crops of linseed, potatoes, sugar beet, and rapeseed, with reports on the development of vines, olive trees, and sericulture in various countries of the Northern Hemisphere.

The portion of the *Bulletin* devoted to agriculture concludes with supplementary information on the 1915 crops in Spain, France, Canada, the United States, Japan, British India, and Algeria, together with data from Uruguay on the crop of 1915-16.

In the commercial portion of the *Bulletin* appear the usual tables of imports, exports, stocks, and prices in the principal markets of cereals and cotton.

It includes also many data as to the rates of ocean freight on the most important routes, both for cereals and cotton.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 8, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Further Determinations of Direct Osmotic Pressures." By The EARL OF BERKELEY, F.R.S., and E. G. J. HARTLEY.

In this communication the osmotic pressures of the following substances are measured directly:—Cane-sugar and methyl glucoside, a number of ferro- and ferricyanides, and one or two other salts. The cane-sugar determinations were made on a somewhat purer sugar than was the case in our previous work; the results extend over the range already covered by Prof. Morse and his co-workers, and the two sets of numbers are found to differ slightly at the lower concentrations.

For the ionised substances examined it may be stated that, with the exception of one salt, all those having a molecule made up of a dyad base combined with a dyad acid radicle are associated in aqueous solution.

The "dynamic" method of measuring osmotic pressures is developed so as to afford a means of rapidly estimating molecular weights to a considerable degree of accuracy even in very dilute solution.

"Magnetic Shielding of Large Spaces, and its Experimental Measurement." By Prof. E. WILSON and Prof. J. W. NICHOLSON.

1. The magnetic shielding of a large space is a problem wholly different in practice from that of a small space, and in view of important applications the efficiency to which much shielding can be raised is a matter of importance. Considerations of mobility of the apparatus and weight of iron required necessitate the solution of the problem of maximum shielding for a given weight of iron and more than two shells, together with an examination of the limitations of utility of lamination. These problems are discussed in the paper.

2. A field of order as low as 3×10^{-3} has been obtained in a space of radius 30 cm. by the use of 1273 kilos. (2806 lbs.) of high-permeability dynamo magnetic steel, and an accurate method designed for the measurement of fields of lower order.

3. The leakage through air spaces in a magnetic shield has been studied.

4. It is now possible to examine the behaviour of iron under practically no magnetic force.

"Motion of Solids and Fluids when the Flow is not Irrotational." By G. I. TAYLOR.

The paper deals with the motion of solids in rotationally moving fluids, a problem which has not apparently engaged the attention of mathematicians before.

The motion of cylindrical solids in rotating fluids is discussed, and it is shown that a solid cylinder of the same density as the fluid will move through a rotating fluid exactly as if the fluid were not rotating. On the other hand, a solid sphere of the same density as the fluid will be deflected to the right if the fluid is rotating anticlockwise and to the left if it is rotating clockwise.

This property of rotating fluids is demonstrated experimentally by means of experiments performed with a rotating tank full of water. It is shown experimentally that vortex rings move in circles through a rotating fluid.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, June 7, 1916.

Mr. GEORGE EMBREY, President, in the Chair.

THE following papers were read:—

"Potash and other Mineral Fertilisers and Constituents of Plants." By R. R. TATLOCK, F.I.C., and R. T. THOMSON, F.I.C.

The composition of the tomato and the chrysanthemum as regards potash, lime, magnesia, and phosphoric acid, and the large excess of the first of these, especially in the tomato, is first dealt with. It is then pointed out that manures of practically the same composition are sold for root crops rich in potash and for cereals rich in phosphoric acid. Analyses of bracken and other plants as sources of potash are given, and the improbability of such extraction being a financial success is stated. Finally, complete analyses of various minerals and rocks are given, the special object being to show the percentage of potash.

"Determination of the Reichert and Polenske Figures of Butter and Margarine using small Quantities of Fat." By A. DOUGLAS HEYWOOD, F.I.C.

The author has determined these figures on $2\frac{1}{2}$ grms. of fat, and finds that under specified conditions there is a constant relation between them and those figures given by 5 grms. of fat, the ratios being $1/1.99$ for the Reichert figure and $1/2.18$ for the Polenske figure.

"Calorific Valuation of Coal without a Calorimeter." By H. PROCTER SMITH, F.C.S.

The author by means of Goutal's formula shows how, from the proximate analysis, the calorific value of a fuel can be calculated, yielding results within the limits of experimental error of the calorific determination, and more trustworthy than many of the figures obtained with some of the cheaper types of instruments.

From the figure thus obtained and the price of the fuel, keeping the different grades separate, a very reliable comparison can be made of the various fuels used and their relative heating value to the consumer.

The methods for the proximate analysis are given, and a description of the mechanical condition of the fuel obtained by screening quantities of about 10 kgrms. weight over 18" diameter sieves of various grades, thus giving additional information of use both to the user and seller of the coal.

"Estimation of Pentose and Pentosans by means of Fehling's Solution." By J. L. BAKER, F.I.C., and H. F. E. HULTON, A.I.C.

The paper deals with the method of Eynon and Lane based on Flohil's process. Analytical details are discussed and modifications for the improvement of the process are suggested, the chief of which are:—

1. The heating of the furfural and Fehling's solution in a water-bath in place of boiling directly over a flame.
2. The employment of a considerably larger volume of Fehling's solution.

The value of the method for the estimation of furfural is confirmed, as are also the values found for the copper-furfural ratio recorded by Eynon and Lane.

SOCIETY OF CHEMICAL INDUSTRY
(LONDON SECTION).

Ordinary Meeting, June 5, 1916.

Mr. ARTHUR R. LING in the Chair.

THE following papers were read:—

"The Action of Nitric Acid on Aluminium." By RICHARD SELIGMAN and PERCY WILLIAMS.

In recent years the use of aluminium in factories making nitric acid and explosives has grown to large proportions, the chief directions in which the metal has found application being the following:—(1) For the conveyance of nitric acid in tanks or by pipelines; (2) for storage and blending in tanks; (3) for carrying off fumes by means of hoods, domes, and vapour pipes; (4) for the covers of vessels, themselves not made of aluminium; (5) for the gigantic pipe systems used in the manufacture of nitric acid from the atmosphere; (6) for many small utensils.

It is therefore essential that the interaction of aluminium and nitric acid on the one hand and of aluminium and nitrating mixtures on the other should be fully understood, and as, moreover, the experience of different factories which have used aluminium has varied within wide limits, it has become a matter of urgent importance to establish as far as possible the causes of these divergences. The present paper is an attempt to explain the conflicting results hitherto obtained in practice. The main conclusions reached were the following:—

Effect of Temperature.—The most important condition affecting the rate of dissolution of aluminium in nitric acid is temperature. Over a considerable range of temperature an increase of 10° C. is sufficient to increase the rate of dissolution by 100 per cent. By attention to this factor the life of aluminium vessels used for the storage or transport of nitric acid can be greatly increased.

Effect of Concentration.—Next to temperature concentration plays the most prominent part in determining the rate of dissolution of aluminium in nitric acid. The most active solvents are mixtures containing between 20 and 40 per cent by volume of nitric acid of 1.42 specific gravity, whilst on the other hand some acids made from the atmosphere and containing 94.7 per cent of HNO_3 were found to be almost without effect on aluminium. A sample of the metal suspended in this acid for seventy-one days lost only 0.0004 grm., equivalent to a dissolution of 0.015 mgrm. of aluminium per 100 sq. cm. per twenty-four hours. The extreme inactivity of acid of this strength is held to account for the great success which has attended the use of aluminium transport vessels by the Norwegian makers of nitric acid.

Impurities in the Nitric Acid.—The presence of up to 0.05 per cent of chlorine in the nitric acid was not found to affect the rate of attack of the latter upon aluminium. Similarly no acceleration could be noted on the addition of 0.01 per cent of iodine. On the other hand the presence of a trace of sulphuric acid was found to promote the rate of attack, 0.04 per cent being sufficient to raise the rate of dissolution by about 70 per cent.

Effect of Oxides of Nitrogen.—The rate of attack is increased by the presence of the lower oxides of nitrogen. If the acid be kept free from such lower oxides the rate of attack on aluminium can be reduced considerably. The effect of the oxides of nitrogen produced by the interaction of nitric acid and aluminium in stimulating the attack is held to account for the fact often observed in practice that dissolution is most rapid in crevices or corners where the acid cannot circulate freely, and where such products therefore accumulate.

Effect of Physical State of the Metal.—The effect of the physical state of the aluminium is considerable, the metal being attacked very much more readily when amorphous than when crystalline.

The Composition of the Metal.—The composition of the aluminium is of very much smaller importance than

has heretofore been assumed to be the case. Nevertheless the purer metal is generally the more resistant to the attack of nitric acid.

The Action of Mixed Acids.—Mixed nitric and sulphuric acids attack aluminium very much more readily than pure nitric acid, and the statements to the contrary to be found in the literature of the subject are erroneous.

Uniformity of the Action.—The attack by nitric acid on aluminium sheet of high quality is absolutely uniform, and during the present investigation no instance of local action or "pitting" has been observed.

Conclusion.—The practical conclusion to be drawn from the experiments described in this communication is that, as the authors have frequently pointed out, aluminium can be used with great advantage for dealing with strong nitric acid provided that the latter be cold and provided that the plant or apparatus be suitably designed. For hot nitric acid of any concentration aluminium can have but a very limited life. Dilute nitric acid if cold could in many cases be handled in aluminium with success, although the life of the aluminium will not be so long as where the metal is exposed only to the action of the strong acid. Owing to the higher rate of attack by dilute nitric acid storage and transport tanks after being emptied should either be washed out thoroughly or so sealed that moisture cannot get in and so dilute the acid which remains in the tank. Finally aluminium should only be used with great caution for handling mixed acids, and where aluminium covers and domes are used above vessels containing such mixtures care should be taken to prevent splashing of the contents upon the aluminium.

DISCUSSION.

Dr. W. R. HODGKINSON said that he had also noticed the brown deposit formed by the action of nitric acid on aluminium. The same kind of deposit was obtained by the action of caustic soda, say, 20 per cent sodium hydroxide solution. It contained silicon and also iron. The evolution of hydrogen was practically stopped by the deposit. He suggested that hydrazine was a better destroyer of the lower oxides of nitrogen than urea.

Prof. H. E. ARMSTRONG, after complimenting the authors on the value of their paper, asked for some explanation concerning the protection of aluminium from the action of nitric acid. Was it due to the formation of a coating of oxide? He hoped Dr. Seligman would continue his experiments, especially with regard to the action of caustic soda on aluminium and the behaviour of aluminium couples. For example, what the effect would be of coupling up aluminium under different conditions with a negative metal such as platinum.

Mr. W. F. REID said that the earlier experiments on aluminium had been made with that produced by the sodium process, which might account for some of the discrepancies between Deville's results and those of the authors.

Dr. SELIGMAN, in reply, said that he thought the film produced by the action of nitric on aluminium consisted largely of silicon. He had not tried hydrazine as a remover of the lower oxides of nitrogen.

Messrs. William Toogood, Limited, sent an exhibit of glass ware made by Messrs. Wood Bros. Glass Co., of Barnsley, Yorks.

Speaking on the subject of the manufacture of glass in this country, Mr. Weldon, a member of the Society resident in Natal, said that since the war they had been very short of chemical glass in that particular colony, into which was imported £34,000 worth in 1912.

"Bacterised Peat." By Prof. W. B. BOTTOMLEY, M.A. The humus of the soil is one of the most essential factors of soil fertility, providing not only food and energy for the soil bacteria, but also serving as a direct source of food for plants. Owing to the diminishing supply of stable manure the question of how to replenish the humus of the soil is a serious one for those engaged in intensive culture.

Peat is rich in humus chiefly in the form of insoluble

humic acid. In a manure heap two kinds of bacterial action are at work—*anaerobic* acting chiefly on carbohydrates, and *aerobic* acting on the nitrogenous constituents. In the water-logged conditions of peat formation the anaerobic action predominates, resulting in the formation of humic acid. When peat is submitted to the action of certain aerobic bacteria at a temperature of 26° C., it is rapidly decomposed, the humic acid is converted into soluble humates, and certain growth-stimulating substances (auximones) are produced similar to the accessory food substances which have been shown to be necessary for animal nutrition.

The auximones which are present in the phosphotungstic acid fraction obtained from an alcoholic extract of bacterised peat are beneficial in two directions:—(1) They stimulate the activities of both the nitrifying and the nitrogen-fixing bacteria of the soil; (2) they have a definite action on plant nutrition. Lemna plants grown in Detmer's complete culture solution with the addition of the phosphotungstic auximone (17 parts per million of culture solution) multiplied rapidly, and retained their size and vigour throughout an experiment extending over three months. Similar plants grown in Detmer's solution alone reproduced slowly, and soon showed signs of starvation, their size diminishing week by week until at the end of the experiment they were about one-fifth their original size. Microscopic investigation showed striking differences in internal structure between the two sets of plants, and suggest the probability that auximones have a specific action on cell metabolism and the nutrition of the nucleus.

DISCUSSION.

Dr. J. A. VOELCKER said that the question raised in the paper, namely, the conversion of vegetable products into plant food, was an important one for chemical industry. When the enormous amount of vegetable matters lying dormant on the land was considered, the question of rendering them available as plant food was one of great importance. They all know that peat contained a large amount of nitrogen, and yet for some reason or other the nitrogen was not available for the nutrition of plants. He had obtained the same results as Prof. Bottomley under greenhouse conditions, but he had failed up to the present to get corresponding results on a field scale.

Prof. H. E. ARMSTRONG asked whether any experiments were being made at Kew in which the effect produced by treated and untreated peat respectively had been contrasted.

Dr. E. H. TRIPP asked whether bacterised peat had any fungicidal value. He did not think that the conversion of a huge bog of peat into bacterised peat was a practical problem, because the peat was absolutely waterlogged, and they could not get the necessary conditions for the growth of aerobic bacteria.

Prof. BOTTOMLEY briefly replied.

NOTICES OF BOOKS.

The Alcohol Industry: Millions Lost to the National Wealth. By T. W. FIRTH CLARK, F.C.S.

The modification of the present regulations of the excise law so that the measures taken to limit the consumption of intoxicants should not be allowed to interfere with the production of alcohol for industrial purposes is an urgently needed reform, and in particular the removal of restrictions as to the methods employed in the manufacture of alcohol cannot be longer delayed if the industry is to survive foreign competition. The author of this pamphlet, which has been issued by Messrs. E. T. Pearson and Co., Ltd., of Mitcham, Surrey, points out in it that by adopting new methods of manufacture foreign countries have been enabled to save more than a fourth of the total cost of raw material, fuel, and labour, and he urges that English distillers should be allowed to economise in the same way.

This would involve the abolition of the regulations regarding the saccharometer test and the use of the alcoholometer for the determination of the total quantity of alcohol produced. The conversion of starch into sugar and sugar into alcohol could be made to take place in the same vat, and distillers could thus use their fermenting and distilling plant simultaneously. The Boulard process, which has made this simplification possible, has been working successfully for some time on the Continent, and English distillers would undoubtedly be enterprising enough to adopt it if it were not for the excise regulations. The author claims for the process that by introducing it distillers could produce three to four times the quantity of alcohol they are now able to manufacture. Thus, millions of pounds would be saved to the country, and distillers could secure a large proportion of the world's trade in alcohol.

Extraction and Recovery of Radium, Uranium, and Vanadium from Carnotite. By CHARLES E. PARSONS, R. B. MOORE, S. C. LIND, and O. C. SCHAEFER. Washington: Government Printing Office. 1915. Pp. 124. Price 25 cents.

THIS bulletin of the Bureau of Mines contains an account of the circumstances which led to the formation of the National Radium Institute, and the objects of the investigation undertaken under the co-operative agreement between the National Institute and the Bureau of Mines are explained. These objects were, firstly, to ensure that the miner and prospector received an equitable return for his ores, and, secondly, to convince the public that the radium resources of the public lands of the United States should be mined under Government supervision. Although their aims have not been fully realised, the investigation has led to the acquisition of valuable knowledge as to the costs of production and recovery of the by-products. Methods of treating the ore which have been worked out by various investigators are first discussed, some new methods being suggested as being worth investigation. The Bureau of Mines process and plant are then described in full detail together with methods of refining and measurement suitable in different cases.

Trattato di Chimica Analitica Applicata. ("Treatise on Applied Analytical Chemistry"). By Prof. VITTORIO VILLAVECCHIA. Volume I. Milan: Ulrico Hoepli. 1916. Pp. xx.+622. Price L.12.50.

THIS treatise deals exhaustively with methods of analysing the principal industrial and food products, and will be valued by Italian chemists as providing them with a reliable and authoritative work on the subject. The methods described include those which have been found most useful for practical purposes, and have been collected from all sources. The subjects treated in the first volume include water for drinking and industrial purposes, chemicals, manures, cements, metals, and alloys. Methods of detecting impurities and adulterations are very fully described, and electrolytic processes are given. The examination of fuels, including calorific determinations, is also discussed, and the analysis of lubricants and fatty substances generally.

Thirteenth Annual Report of the Director of the Bureau of Science, Philippine Islands. By ALVIN J. COX. For the Year ending December, 31, 1914. Manila: Bureau of Printing. 1915.

THE Bureau of Science of the Philippine Islands has earned an enviable reputation owing to the excellent quality of the work which has issued from it, and the thirteenth report shows that in spite of many difficulties it is in no danger of losing its place among research institutes. The staff has been unavoidably decreased, but by extra effort upon the part of those still at work the routine work has been kept pace with and a certain amount of research done. The Bureau has always been under efficient and

vigorous management, and the many publications which have emanated from it show the value of its labours. The results which have been collected have led to a great improvement in the health conditions of the islands, and commerce and industry are directly benefiting; thus in the chemical laboratory it has been proved that the clays and shales of the islands are suitable for brickmaking and similar purposes, and by the same department simple and economical modifications of local tanning methods have been worked out.

CORRESPONDENCE.

SULPHATE OF AMMONIA.

To the Editor of the Chemical News.

SIR,—We enclose copy of an article which has just appeared in a German paper, which gives a forecast of the position of nitrogen in Germany next year.

We cannot vouch for the accuracy of the estimates presented, and one or two of the statements appear obviously exaggerated. We think, however, that the article shows clearly that the increase in production of nitrogen in Germany is likely to prove larger than has hitherto been expected. This makes it all the more necessary that every effort should be made to cultivate and develop the home market for sulphate of ammonia in this country.—I am, &c.,

D. MILNE WATSON,

Chairman of the Sulphate of Ammonia Association.

84, Horseferry Road, Westminster,
June 12, 1916.

THE GERMAN NITROGEN INDUSTRY AND THE FUTURE OF GERMAN AGRICULTURE.*

During the last ten years German agriculture has succeeded in increasing the yield of the land to an extraordinary extent, and in this connection a comparison with France is of interest.

Thirty years ago the yield per hectare in France was about the same as in Germany. Since then the yield in France has risen about one-tenth, whereas Germany has nearly doubled her yield, as the following table shows:—

Wheat Yield per Acre in 100 kilograms.

Yearly average.	1881-1886.	1911-1913.
Germany	12.8	22.3
France	12.0	13.6
Russia	?	6.9

This excellent result is due to the development partly of the farmers' associations, of agricultural schools, and the employment of modern methods, but chiefly to the ever-increasing quantities of fertilisers used. The following is a comparison of the amounts of fertilisers used per hectare during the last few years:—

	Potash.	Nitrate of soda.
Germany ..	12.05 kilogram.	8.10 kilogram.
France ..	0.806 „	4.10 „

Germany has always been well provided with potash, but up to about ten years ago had to rely almost entirely on imports of nitrate of soda for her nitrogen. The following table shows the increase in the imports of nitrate, and in this connection it should be mentioned that about 10 to 15 per cent of these quantities have been used for industrial purposes.

Gradually, however, the German chemical industry has been building up a substitute for nitrate in the form of sulphate of ammonia. At the beginning of this century the production in Germany was still small and imports amounted to about 48,000 tons per annum. Since 1906,

however, things have changed and Germany has exported larger quantities than she has imported.

German Consumption of Nitrate of Soda.

	Tons.	Value (Mill. £).
1880.. .. .	55,000	?
1885.. .. .	155,000	1½
1890.. .. .	330,000	9½
1901.. .. .	517,000	4½
1910.. .. .	723,000	6½
1911.. .. .	703,000	6½
1912.. .. .	785,000	8½
1913.. .. .	747,000	8½

The development of our consumption of sulphate of ammonia is shown by the following table:—

German Consumption of Sulphate of Ammonia.

	(Tons in Thousands).					
	1888.	1900.	1909.	1910.	1911.	1913.
Imports.. . . .	35	23	58	31	24	35
Exports	—	2	59	93	74	76
Excess of imports over exports ..	35	21	—	—	—	—
Excess of exports over imports ..	—	—	1	62	50	41
Production from coke ovens, &c.	?	104	281	313	418	501
Total consumption	—	125	280	251	368	460

The increase in the use of sulphate of ammonia has, therefore, been extraordinarily rapid. In the year 1913 460,000 tons of ammonia were used as against 750,000 tons of nitrate of soda. Taking the manual value of sulphate compared with nitrate as 4 to 3, the 460,000 tons are equal to 610,000 tons of nitrate, so that the two competitors were running each other pretty close already in 1913.

In 1914 synthetic sulphate of ammonia first entered the lists as a competitor of nitrate of soda on a practical scale. Theoretically the possibility of producing ammonia by purely chemical means had long been known, and the well-known Norwegian method was first of all developed, the German chemical trade being largely interested.

The difficulties of introducing this process into Germany on account of the lack of water power forced the Badische Aniline and Soda Works to develop a process of their own. In conjunction with Prof. Haber they proceeded to do this, putting all their energy into the Haber process and giving up their Norwegian interests.

At the beginning of the war the Badische were producing on a scale large enough for one single works, but yet not sufficiently large to compensate for the loss of nitrate of soda. In the first year of the war there was accordingly a considerable shortage of fertilisers for agricultural purposes. But our chemical industry quickly came to the rescue, and should the blockade of Germany be prolonged we should soon be in a position to deliver more nitrogen for agricultural purposes than agriculture consumed in peace times.

The following particulars give an idea of the extraordinary rapidity with which the Haber process has developed. The production rose from 30,000 tons in 1913 to 60,000 tons in 1914, and about the middle of 1915 the output of the original works was about 150,000 tons. From 1916 onwards the production is reckoned at 300,000 tons. It is no secret that the Badische Company has lately begun putting up further large plants in another part of Germany, so that its producing capacity from 1917 onwards will no doubt be considerably in excess over that of 1916.

Assuming that the Haber production in the near future will amount to 500,000 tons this process alone will represent the production of an amount of nitrogen very nearly equal to the amount of nitrate of soda we used to import. In passing we may mention that such a production at a price of £12 10s. per ton would represent an annual turnover of 6½ million £ sterling for this one firm.

* From the *Frankfurter Handelsblatt*, May 29, 1916.

Added to this, however, is the fact that with State aid further large quantities of nitrogen have been produced in the form of nitrate of lime, with the help of which our agricultural needs can easily be met. In addition, the whole tendency in the coal industry has been towards increasing the development of by-products. Up to the time when the war broke out about one-fifth of our coal was coked, but to-day the war has forced us to resort to coking to a far greater extent than before, and everything points to the conclusion that in the near future the direct combustion of coal will be recognised as altogether uneconomic and disappear and its place be taken by by-product processes. This of course means increased recovery of ammonia from coal. Assuming that only double the quantity of coal hitherto used is employed for the recovery of ammonia the increase in the sulphate of ammonia production would amount to 450,000 tons. Basing on the above, we can make the following comparison between 1913 and 1917:—

German Consumption of Nitrogen, 1913.

	Tons.	Tons nitrogen.
Sulphate of ammonia.. ..	460,000	= 92,000
Norwegian nitrate of lime..	35,000	= 4,500
Nitrate of lime	30,000	= 6,000
Ammonia — Haber process	20,000	= 4,000
Total		106,500
Plus nitrate of soda	750,000	= 116,000
Grand total		222,500

German Production of Nitrogen, 1917.

Sulphate of ammonia.. ..	700,000	= 140,000
Norwegian nitrate of lime..	—	—
Nitrate of lime	400,000	= 80,000
Ammonia — Haber process	500,000	= 100,000
Total		310,000
Nitrate of soda		?

If these estimates are only approximately correct our own production will already next year be greater than our consumption before the war, including the amount of nitrate of soda imported. In case of need, therefore, we can do without the importation of nitrate of soda for agricultural purposes altogether. This does not mean, however, that the import of nitrate of soda is either unnecessary or undesirable. Nitrate will remain very much wanted for certain purposes, and agriculture will be glad to make use of it as long as prices remain competitive, especially seeing the amount of German capital invested in the nitrate of soda business. If our home production of nitrogen can be supplemented by nitrate of soda so much the better, for our experts are agreed that we cannot give our agriculture enough nitrogen. The dire necessity which this war has brought upon us, forcing us to help ourselves in all sorts of ways, has in this respect given us a valuable gift for the future, seeing that the new sources of nitrogen will enable us to increase our agricultural production.

All sorts of possibilities are involved in this. It would be thoroughly in keeping with the character and the accomplishments of German chemical industry to proceed with the production of combined fertilisers after having successfully solved the problem of synthetic production of ammonia. These manures will perhaps one day drive out the old fertilisers in the same way as synthetic indigo drove out the natural product.

It is not impossible that Germany may one day become the great exporter of nitrogenous fertilisers. The most important point, however, is the increase in the productivity of our land. The economy of £9,000,000 per annum on nitrate of soda imports cannot be compared in importance with the saving in our imports of wheat and foodstuffs which would be effected by means of increased fertilising.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxix. No. 18, May 1, 1916.

Catalysis of Hydrogen Peroxide in Heterogeneous Medium. Second Part. Experiments with Platinum.—Georges Lemoine.—Distilled hydrogen peroxide was kept at constant temperature in presence of platinum black and platinum sponge, and the volume of the gas evolved was measured. It was found that the velocity of the reaction increases very rapidly with the weight of the catalyst and with its state of division. When the volume of hydrogen peroxide is increased, other things being equal, the volume of gas liberated increases, but not indefinitely. The comparison of platinum black and platinum sponge, in the same state of division, shows that the former has a special catalytic action, much more energetic and due to a distinct cause.

Absolute Density of Gaseous Hydrobromic Acid.—E. Moles.—Hydrobromic acid was obtained by two methods; firstly, by the reaction $\text{Br}_3\text{P} + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HBr}$, and, secondly, by the reaction $\text{Br}_2 + \text{H}_2\text{S} = \text{S} + 2\text{HBr}$. In both cases the excess of bromine was removed by cooling, and after having been dried the gaseous HBr was condensed by means of liquid air and fractionally distilled. The mean value of the density was then found to be 3.644 grms. per normal litre.

Bulletin de la Société Chimique de France.

Vol. xix.-xx., No. 4, 1916.

Contribution to the Study of Barium Oxalate.—Echsnér de Coninck.—The author has proved the existence of four hydrates of neutral barium oxalate:— $\text{C}_2\text{O}_4\text{Ba} + 3\text{H}_2\text{O}$, $\text{C}_2\text{O}_4\text{Ba} + 2\text{H}_2\text{O}$, $\text{C}_2\text{O}_4\text{Ba} + \text{H}_2\text{O}$, $\text{C}_2\text{O}_4\text{Ba} + \frac{1}{2}\text{H}_2\text{O}$. The optimum temperature for the production of the trihydrate is 8 to 10°, that of the monohydrate 15 to 18°, and the dihydrate 22 to 25°. The hemihydrate is formed by the action of a boiling solution of oxalic acid on barium carbonate or nitrate. Although the temperatures of formation of mono and dihydrate are very different the two salts are often precipitated together. One hydrate of the acid oxalate exists, namely, $(\text{C}_2\text{O}_4\text{H})_2\text{Ba} + 2\text{H}_2\text{O}$. This dihydrate is very unstable, being easily decomposed by water into the neutral oxalate and oxalic acid.

Probable Identity of Laurent's Indin with Wahl and Bagard's Iso-indigo.—Léon Lefèvre.—Laurent prepared a substance which he called indin by the action of heat on isathyde, or the action of potash upon isathyde sulphide. He attributed to it the formula $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$. The same substance was afterwards obtained by Knop by dehydrating dioxindol. More recently, Wahl and Bagard obtained iso-indigo by the condensation of oxindol with isatin, and the author believes that iso-indigo and indin are identical. He bases this opinion upon the similarity of the reactions by which they are formed and upon the general resemblance of their properties. Thus they are both red substances, insoluble in water, and very slightly soluble in alcohol and ether, soluble in concentrated sulphuric acid, giving a red solution.

MEETINGS FOR THE WEEK.

THURSDAY, 29th.—Royal Society. "Genesis of Pleochroic Haloes," by J. Joly. "Determinations of the Sign and Magnitude of Electric Discharges in Lightning Flashes," by C. T. R. Wilson. "Further Observations on Protozoa in Relation to Soil Bacteria," by T. Goodey. "New Bennettitean Cones from the British Cretaceous," by M. C. Stoppel.

THE CHEMICAL NEWS

Vol. CXIII., No. 2953.

AN EASY METHOD FOR DETERMINING VAPOUR-DENSITIES.*

By PHILIP BLACKMAN.

SEVERAL lengths (3 or 4 metres) of capillary tubing, of as uniform bore throughout as possible, are fused together, and the whole bent into a flat spiral to present as compact a form as can be (Fig. 1). A short thread of mercury, as near as possible 10 mm. in length, is introduced at one end, and forced through the tube by aid of a pump, and file marks scratched on the tube corresponding to the successive lengths of this mercury thread, and these will serve as a graduation of the bore in lengths in terms of the

tube is placed horizontally, the end A unsealed, and the length l of the thread of liquid D is measured in terms of the graduation on the tube. The specific gravity (density) s of the liquid must be determined. The apparatus is heated in a horizontal position in a suitable heating vessel to a temperature t_2° C. to cause the substance to vaporise completely. The heating should be gradual so that the evaporating liquid slowly pushes the mercury thread, C, outwards towards the end A; if the heating be sudden the force of the suddenly expanding vapour may cause the mercury thread C to be ejected from the tube. When the expanding vapour has attained the stable condition (C remaining stationary) the length L between the mercury threads (in terms of the graduations on the tube) is now read off, and if p be the external atmospheric pressure (mm.) the vapour-density d is calculated from the formula—

$$d = \frac{31068 \cdot sl}{pL} (273 + t_2)$$

Of course this apparatus cannot be used with substances which (or whose vapours) react upon mercury. At high temperatures p must be written $p-q$, where q is the



FIG. 1.

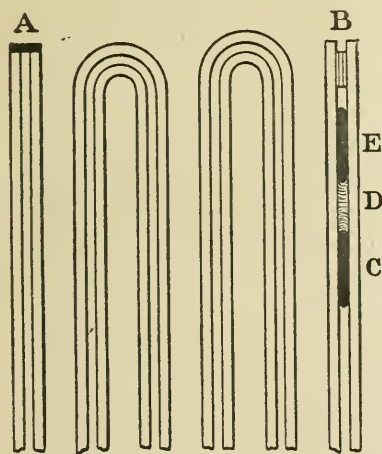


FIG. 2.

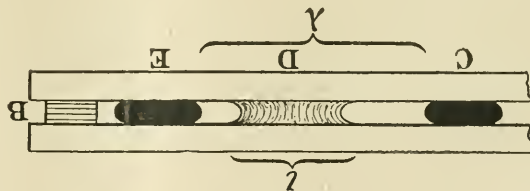


FIG. 4.

FIG. 4.

mercury thread's length; this graduation is necessary as the bore will not be of perfectly uniform width, especially at the bends and joints.

The tube is placed with the open ends upwards (Fig. 2), and one end, A, is temporarily closed, with a piece of gummed paper for instance. A piece of ordinary tubing is drawn out to a fine point at one end (Fig. 3) to act as a refill, and a little mercury is drawn up it and introduced into the open end, B, of the tube in the position C. This same refill is now used for introducing similarly a short thread (4 to 10 mm.), D, of the liquid whose vapour-density is to be determined, C and D being contiguous. Then a second thread of mercury, E (contiguous to D), is likewise inserted, after which the open end B is sealed up by aid of a suitable cement (e.g., putty), or better closed by fusion. The

vapour pressure (mm.) of mercury at the particular heating temperature t_2° C. No great degree of accuracy is claimed for this apparatus.

It was stated above that the threads, C, D, E, must be contiguous to exclude air. But this need not be so if the following allowance in the calculation be made for the contained air. Thus (Fig. 4), let λ represent the distance between the mercury threads, then (if a be the area of the cross-section of the bore) $(\lambda - l)a$ is the volume of the contained air at t_1° C. and pressure p mm. which, at t_2° C. and pressure p mm. (assuming that the latter has not changed), has a volume equal to—

$$\frac{(\lambda - l)a(273 + t_2)}{273 + t_1}$$

and hence the volume of the vapour is equal to—

* Compare *Journal of Physical Chemistry*, 1909, xiii., 606.

$$L_a - \frac{(\lambda - l)a(273 + t_2)}{273 + t_1};$$

therefore its specific gravity is—

$$s_{1a} \div \left\{ L_a - \frac{(\lambda - l)a(273 + t_2)}{273 + t_1} \right\},$$

or if compared with that of hydrogen at 0° C. and 760 mm. pressure (assuming that 1 grm. of hydrogen occupies 11160 cc.),—

$$11160 s_{1a} \div \frac{273p}{760} \left\{ L_a - \frac{(\lambda - l)a(273 + t_2)}{273 + t_1} \right\}$$

from which on simplification—

$$d = \frac{31068 sl(273 + t_2)(273 + t_1)}{p[L(273 + t_1) - (\lambda - l)(273 + t_2)]}.$$

(It will be seen that if $\lambda - l = 0$, that is if no air be enclosed between c and e, this formula reduces to the former one).

Solids of low boiling-point can also be dealt with in this apparatus. After the introduction of the first mercury thread the crushed solid is pushed in close to the mercury, and the tube just here gently warmed to cause the solid to just melt and run together upon the mercury, when it is allowed to solidify and cool, and then the second mercury thread is introduced.

It will be found more satisfactory perhaps and less troublesome, instead of graduating the tube, to determine simply the initial and final volumes (after making the necessary positions) corresponding to $L, l, (\lambda)$, by filling the respective bore-lengths with mercury and determining the weights of the mercury threads from which the volumes can be calculated (the calculation of the volumes is really unnecessary); for if w, W, w_λ represent the mercury weights corresponding to l, L, λ , respectively, and g the specific gravity of mercury, then evidently $la = w/g$, $La = W/g$, and $\lambda = w_\lambda/g$, or $l = w/ga$, $L = W/ga$, $\lambda = w_\lambda/ga$, and substituting these values in the two formulæ we get—

$$d = \frac{31068 sw(273 + t_2)}{pW}$$

and—

$$d = \frac{31068 sw(273 + t_1)(273 + t_2)}{p[W(273 + t_1) - (w_\lambda - w)(273 + t_2)]}.$$

Hackney Technical Institute, London, N.E.

HEXABROMODIACETYL.*

By C. LORING JACKSON and ROGER ADAMS.

(Concluded from p. 295).

Experimental.

Preparation of Hexabromodiacyl, $\text{CBr}_5\text{COCOCBr}_3$. (This substance was supposed by Fiske and one of us to be heptabromomethyldiacetyl (*Am. Chem. Journ.*, 1913, 1, 360); see the introduction to this paper).—The process used by us differs in some important details from that described in the previous paper, and is therefore given in full. 200 grms. of sodium hydroxide were dissolved in a litre of water, and after cooling to a few degrees above zero, 100 grms. of tetrabromo-*o*-quinone were added in small portions at a time with constant shaking. If impure orthoquinone was used, the same product was obtained, but the yield was materially lowered. The green colour, which appeared at first, gradually changed to brown, and at the same time enough gas was given off to cover the surface of the solution with foam. The mixture was allowed to stand in ice for two to three hours, and then at room temperatures for about five hours, after which it was poured into 400 cc. of strong hydrochloric acid (more than enough for neutralisation) slowly and with constant cooling, so that

the temperature of the mixture should never rise above luke-warm. The yellowish brown flocculent precipitate of tetrabromopyrocatechin formed in this way was filtered off after settling for five to ten minutes. To the filtrate were added 2 cc. of bromine, and the mixture shaken until it was entirely absorbed. This treatment was repeated till the presence of an excess of bromine was shown by the reddish colour of the liquid, which required 23–25 cc. if the tetrabromo-*o*-quinone was pure, 13–18 cc. if it was crude. During the treatment with bromine the red liquid became at first milky, then began to give off carbon dioxide, and toward the end of the process a yellow precipitate appeared. In five to ten minutes after the end of the treatment this precipitate had settled, when it was filtered out and allowed to stand on a porous plate until thoroughly dry, which took about a day. An additional amount of decidedly impure product was obtained by allowing the filtrate to stand overnight with 5 cc. of bromine. The dry precipitate was powdered, and extracted with successive portions of petroleum ether (boiling 30–50°) until the yellow substance was completely removed leaving a brown tarry impurity. Upon distilling off the larger part of the petroleum ether and cooling the residue, the hexabromodiacyl crystallised out in a pure state, as shown by its melting-point 100–101° (uncorr.), which was not raised by recrystallisation from petroleum ether. (In the previous paper it was given as 97–98°). The yield varied from 21 to 24 grms. from 100 grms. of tetrabromo-*o*-quinone, but fell as low as 12 grms. if crude material was used. The analyses of this substance will be found in the introduction.

Properties of Hexabromodiacyl.—It crystallises from petroleum ether in orange-yellow plates shaped like arrow-heads, and melts at 100–101° (uncorr.) instead of at 97–98° as given in the previous paper. This difference is probably due to the removal of the tarry impurity left after repeated extractions with petroleum ether. It is easily soluble in alcohol, methyl alcohol, ether, benzene, carbon tetrachloride, or glacial acetic acid; slightly soluble in petroleum ether, which is the best solvent for it; essentially insoluble in water. It is very stable toward acids, the three strong acids having no action on it in the cold or on short warming to 100°. Fuming nitric acid when boiling dissolves it, but on cooling the substance crystallises out to all appearance unaltered. Analyses showed, however, that it had lost 1–2 per cent of bromine. Boiling for several hours with strong nitric acid seems to decompose it completely. Boiling with sulphuric acid diluted with its own volume of water gives bromoform, but in such small amount that only a very slight decomposition is indicated. Water, hydric dioxide, or constant boiling hydrobromic acid, while without effect on it in the cold, if heated with it to 100° in a sealed tube for ten days, decomposes it, two of the products in each case being pentabromoacetone and bromoform. This behaviour recalls the formation of pentabromoacetone in a yield of 30–40 per cent from tetrabromodiacyl by the action of hydric dioxide. It is certainly strange that the substance should be distinctly less stable with water than with sulphuric acid. Hydriodic acid or acetone reduces it, as will be described later, and so will the action of potassium iodide.

In the hope of obtaining a dicyanhydrine similar to that yielded by tetrabromodiacyl 15 grms. of the hexabromodiacyl mixed with 2–3 cc. of ether and 40 grms. of a 40 per cent aqueous solution of hydrocyanic acid were heated to 40° under a return condenser. The solid gradually went into solution, and after five to ten hours the two layers of liquid formed at first were converted into a homogeneous mixture, which was allowed to stand overnight, heated for a few more hours in the morning, and after cooling to 0° diluted with its own volume of water and extracted with ether. The dried extract yielded only a yellow oil, which did not solidify on cooling, on standing for a month, and yielded only an oil on saponification with hydrochloric acid at 100°.

Alkaline reagents, on the other hand, decompose it

* *Journal of the American Chemical Society*, xxxvii., No. 11.

easily. The hydroxide of sodium, potassium, or barium even in dilute solution converts it rapidly into bromoform and an oxalate; sodium carbonate acts in the same way, but more slowly. A quantitative study of this reaction made by Fiske and one of us showed that two molecules of bromoform and one of oxalic acid were formed. Hot sodium methylate gave the same result, but in the cold a colourless product melting at about 80° was obtained, which has not been investigated. Boiling with an aqueous solution of sodium acetate also gave bromoform hydrobromic acid and oxalic acid, but when boiled with calcium carbonate and water a sharp odour like that of a bromo-ketone was observed, and only tarry products were obtained. The same odour was produced by boiling with silver and water, but in this case oxalic acid and silver bromide were detected. A mixture of aqueous ammonia and alcohol gave in the cold oxamide, and aniline added to a benzene solution of the diketone gave oxanilid. *o*-Phenylenediamine gave somewhat impure *o*-phenylene-oxamide. Hydroxylamine hydrochloride had no apparent action, phenylhydrazine removed bromine from it, pyridine gave a black tar. No action was obtained with acetyl chloride, or acetic anhydride, or benzoyl chloride. Aqueous sulphurous acid did not act on it, even when standing several months with it. Zinc and acetic acid or aluminium amalgam gave tars in preliminary experiments, but better results were obtained with hydriodic acid, as is described later. Bromine in the cold had no apparent effect upon it, and when heated with it in a sealed tube tarry products were formed. The most interesting behaviour of the diketone is that with alcohols, which is therefore described in detail.

Action of Hexabromodiacyetyl with Alcohols. Hexabromodiacyetylmonomethylhemiacetal, $\text{CBr}_3\text{COC}(\text{OHOCH}_3)\text{CBr}_3$.—This substance was prepared by allowing a solution of hexabromodiacyetyl in methyl alcohol to stand for four to five days. A less pure product was obtained by the aid of heat. Absolute methyl alcohol should not be used in this preparation as it forms an oily substance; in fact, in an experiment which stood for two weeks very little hemiacetal was obtained, the chief product being an unmanageable thick red oil. Even with ordinary methyl alcohol a little of this oil was formed, and therefore after the methyl alcohol had evaporated spontaneously the residue was allowed to stand on a porous plate, after which it was recrystallised from petroleum ether until it showed the melting-point 105° (uncorr.). Analyses of this substance are given in the table in the introduction. Ten grms. of diketone yielded 5 grms. of the hemiacetal.

Properties of Hexabromodiacyetylmonomethylhemiacetal.—Three sorts of crystals of this substance were obtained from petroleum ether, which differed so much in appearance that it certainly crystallises in three different habits if not in three crystalline forms. On cooling or rapid evaporation of the solution most of the crystals are slender long prisms, sometimes with a bluntly pointed end, sometimes with a square end; these turn opaque when exposed to the air, but without loss of weight. The second form consists of short square-ended prisms like slightly elongated cubes, usually bevelled on the edges, more rarely on the ends. These predominate when the evaporation is carried on slowly; but in most crystallisations both forms appear, and one is converted at least partially into the other by recrystallisation. We do not feel certain that these are not different habits of the same crystalline form in spite of the great difference in their appearance. The third sort of crystal, on the other hand, seems distinctly to belong to a different system, for, while we should call the other two forms orthorhombic, or perhaps monoclinic, this third one seems to be tetragonal, since it consists of octahedra modified by many small planes, the two most conspicuous sets either truncating two opposite angles, or else the four edges of the octahedron the opposite angles then being unmodified. The vertical axis is but little longer than that of a regular octahedron, but in no case did we observe similar modifications on all the angles or edges. This

form also has a much more brilliant lustre than the other two. We obtained it only once, and could not again find the conditions under which it is formed. On recrystallisation from methyl alcohol it is converted into the one first described. All three forms contain the same per cent of bromine.

The hemiacetal when crystallised from petroleum ether melts at 105° (uncorr.), but if methyl alcohol is used the melting-point cannot be raised to this temperature, which explains the lower melting-point ($100-101^{\circ}$) given in the earlier paper. This is obviously due to an action of the methyl alcohol upon it, which was also shown by the fact that such a solution although colourless at first turned yellow in a few minutes, but from this solution colourless crystals were obtained. As already stated, absolute methyl alcohol, if allowed to stand with it for some weeks, converts it into a red oil. The most obvious explanation of this action is that the dihemiacetal is formed, but this is rendered doubtful by the fact that the benzene solution also turns yellow on standing exposed to the air, and upon evaporating the benzene solution used in the molecular weight determination the residue was brownish. The crystals show a tendency to turn brown when exposed to the air, especially if moist. This apparent instability is surprising in view of the fact that it offers a strong resistance to the action of acids, strong nitric acid dissolving it apparently unchanged, while it was not decomposed by sulphuric acid diluted with its own volume of water until it has been boiled with it some time. Then it formed an oil smelling like camphor. It is easily soluble in all the common organic solvents except petroleum ether, in which it is less soluble. This is the best solvent for it. It distils slightly with steam. It is unstable toward alkalis since alcoholic ammonia forms ammonium bromide and aniline gives an oil. Hydroxylamine hydrochloride acetic anhydride, or acetyl chloride does not act on it. A methyl alcohol solution boiled with finely-divided silver gives an oil and a few white crystals melting near 70° .

Hexabromodiacyetylmonoethylhemiacetal.—
 $\text{CBr}_3\text{COC}(\text{OHC}_2\text{H}_5)\text{CBr}_3$.

—Ten grms. of hexabromodiacyetyl dissolved in 150 cc. of alcohol were allowed to stand at ordinary temperatures for two to three days, after which the alcohol was allowed to evaporate spontaneously. If the solution was heated the product was less pure. The yellowish white crystals thus obtained, after standing on a porous plate, were crystallised from petroleum ether until they showed the constant melting-point $96-97^{\circ}$. The yield after one crystallisation was 6 grms. The analyses will be found in the table in the introduction.

Properties of Hexabromodiacyetylmonoethylhemiacetal.—It crystallises in narrow plates often 2–3 cm. long terminated by two planes at different angles to the sides, less commonly by one of these planes, so that there is either a blunt or a very sharp end according to which of the planes is present. It turns brown easily when exposed to the air, especially if moist; after this change the percentage of bromine had fallen about 2 per cent. It melts at $96-97^{\circ}$ (uncorr.) instead of $93-94^{\circ}$ as given earlier. It is easily soluble in alcohol, methyl alcohol, ether, acetone, or ethyl acetate; soluble in benzene, chloroform, tetrachloride of carbon, or glacial acetic acid; slightly soluble in petroleum ether, which is the best solvent for it; essentially insoluble in water. It distils with steam, although with difficulty.

When the monoethylhemiacetal was heated in a sealed tube with water to 100° for several days the products were carbon dioxide, bromoform, hydrobromic acid, and probably monoethylloxalic ester, as the diethylester was obtained from it by distillation (Anschütz, *Ber.*, 1883, xvi., 2413).

As this substance could be prepared more easily than the methyl compound it was studied in greater detail, and we tried especially to convert it back again into the hexabromodiacyetyl, but without success. Four experiments were

tried with boiling dilute sulphuric acid, in which the water was allowed to evaporate until the boiling-point had risen from 110–135°, and at this temperature the boiling was continued for some time under a return condenser. The ethyl compound turned slightly yellow, but was recovered unchanged in every case. On heating to 150° for a few hours with strong sulphuric acid the substance was decomposed, forming a dirty yellow solution, but no hexabromodiacytyl could be detected. Boiling with constant boiling hydrobromic acid for three hours or heating with it to 100° in a sealed tube produced no change. This marked stability toward acids is striking in view of the ease with which it decomposes when moist, or when heated with water.

Sodium hydroxide decomposes the hexabromodiacytyl-monoethylhemiacetal giving bromoform and a little oxalate, while barium hydroxide acts in a similar way, but only a trace of oxalate is formed. Sodium carbonate gives over 10 per cent more bromoform than that required for one molecule, but only about half the calculated amount of oxalic acid. Sodium methylate also decomposes it even when used in the proportion of only one molecule. In all these reactions with alkaline substances it was observed that the hemiacetal is distinctly more stable than the diketone. Ammonia or aniline forms only tars, but also acts slowly. Hydroxylamine hydrochloride had no action on it.

Acetic anhydride or acetyl chloride dissolves the hemiacetal, but no reaction takes place even after standing four to seven days. If sodium acetate is used with the acetic anhydride a yellow colour appears, but the slight decomposition is probably due to the action of the salt. When the substance is heated to 120° overnight with acetyl chloride a sweet smelling oil is obtained, which deposits crystals of the unchanged monoethylhemiacetal, but the amount which reacts is so small that we could not study the product. Acetic anhydride when hot also gives an oily derivative. Zinc and acetic acid give small amounts of oil. When the hexabromodiketone is heated with alcohol, instead of reacting with it in the cold, tarry products are obtained with an odour like that of a bromoketone.

Pentabromoacetone.—In the preparation of hexabromodiacytyl the filtrate from it was mixed with 5 cc. of bromine, and allowed to stand overnight; when a red oil was deposited, which changed to a sticky crystalline mass, if it was allowed to stand a few days in an open beaker after the water had been separated. Most of the oil was then removed by a porous plate, and the residue crystallised by the slow evaporation of its solution in petroleum ether. The crystals were partly orange-yellow hexabromodiacytyl, partly a white substance, which was separated mechanically, and after crystallisation from petroleum ether melted constant at 73° (uncorr.). Although the melting-point of pentabromoacetone is 76° our analyses showed that our product is this substance.

Calc. for $\text{CBr}_3\text{COCBr}_2\text{H}-\text{C}$, 7.95; H, 0.22; Br, 88.31; M.W., 453. Found— C , 8.50; H, 0.46; Br, 88.30; M.W., 388, 473, 417.

The same compound was formed by heating hexabromodiacytyl for ten days at 100° in a sealed tube with water, perhydrol, or constant boiling hydrobromic acid; bromoform was also formed in each case.

When hexabromodiacytyl stood for several days with amyl alcohol the product, after being freed from unaltered alcohol by a blast of air, was a yellow oil which to our great surprise contained an amount of bromine only 1 per cent too high for that required by the monoamylhemiacetal.

Pentabromodiacytylmonobenzylhemiacetal.—

$\text{CBr}_2\text{HCOC}(\text{OHOC}_2\text{H}_5)\text{CBr}_3$.

—Five grms. of hexabromodiacytyl were heated on the water-bath in a 25 cc. flask with 5–6 grms. of benzyl alcohol for ten hours. At the end of this time the residue

was distilled with steam, which carried over the excess of benzyl alcohol and the benzyl bromide formed. The yellowish oil, which had not distilled with the steam, was allowed to stand until it had crystallised, and then after being freed from oil with a porous plate it was crystallised from naphtha boiling between 70° and 100°, until it showed the constant melting-point 109–110° (uncorr.). The yield varied from 2–2.5 grms. The analyses given in the introduction show that the substance is the pentabromodiacytylmonobenzylhemiacetal. The hydrobromic acid formed in this reduction was detected in the water with which the product was distilled, and had also converted some of the benzyl alcohol into benzyl bromide as was shown by its violent action on the eyes.

Properties of Pentabromodiacytylmonobenzylhemiacetal.

—It crystallises from ligroin in large thick rhombic prisms, which melt at 109–110° (uncorr.). It is easily soluble in alcohol, methyl alcohol, ether, benzene, or glacial acetic acid; less soluble in ligroin, which is the best solvent for it; essentially insoluble in petroleum ether or water. Strong sulphuric acid, nitric acid, hydrochloric acid, or hydrobromic acid has no apparent effect on it. It is more stable toward alkalis than the hemiacetals of hexabromodiacytyl, as barium hydroxide did not attack it at all even on standing with it for two days, and sodium hydroxide did not decompose it completely until it had stood with it several days. The yellow oil thus obtained contained no bromoform. Acetyl chloride or acetic anhydride has no action on it; in fact, it crystallises very well from the anhydride, the crystals showing the melting-point 109–110°, and containing 67.93 per cent of bromine (calc. for the hemiacetal, 67.92).

Metanitrobenzyl alcohol when heated on the water-bath with hexabromodiacytyl was converted into *m*-nitrobenzyl ether, and this was the only product found, the diacytyl having apparently decomposed completely. Phenol formed with hexabromodiacytyl an unpromising black mass.

Attempts to make hemiacetals by contact with alcohols yielded no results with tetrabromodiacytyl, dibromodiacytyl, diacytyl, benzyl, or pentabromoacetone.

Reduction of Hexabromodiacytyl.—Reduction experiments with zinc and acetic acid, or sulphuric acid yielded only a few drops of oil, but acetone or hydriodic acid gave a better result. Five grms. of hexabromodiacytyl were dissolved in acetone, and allowed to stand four to five hours at ordinary temperatures (longer standing yielded the same product), after which the solution was allowed to evaporate spontaneously under the hood because of the bromoacetone. On standing overnight a hard mass was obtained, which, after removing the last of the bromoacetone by a porous plate, was crystallised from petroleum ether until it showed the constant melting-point 94–95° (uncorr.). This suggested that it was tetrabromodiacytyl, which melts at this temperature. Accordingly, a specimen of this compound was prepared from diacytyl, when it was found to coincide with our product in every respect, the yellow crystals from carbon disulphide being especially characteristic, as they consisted of rhombic plates with the acute angles truncated, and in every case one of these truncating planes was nearer the obtuse angles than the other, giving the crystals the shape of a coffin. For greater certainty our product was analysed.

Calc. for $\text{CHBr}_2\text{COCOHBBr}_2-\text{C}$, 11.94; H, 0.50; Br, 79.60. Found— C , 12.07; H, 0.85; Br, 79.68, 79.58.

Hydriodic acid produced the same substance when 1 gm. of hexabromodiacytyl previously moistened with water was shaken with 2 cc. of the constant boiling acid. After filtering out the iodine the filtrate was extracted with ether or allowed to evaporate. The product was recognised by its melting-point 94–95° (uncorr.) as tetrabromodiacytyl, which is moderately soluble in water.

Pentabromodiacytylmonoethylhemiacetal.—

$\text{CBr}_2\text{HCOC}(\text{OHOC}_2\text{H}_5)\text{CBr}_3$.

—Ten grms. of hexabromodiacytyl dissolved in 150 cc. of

alcohol and 15 cc. of acetone were allowed to stand five to eight weeks at ordinary temperatures. The product, after the solvents had evaporated spontaneously, consisted of two substances, the hexabromodiacylmonoethylhemiacetal and another, which was distinctly more soluble in alcohol, and therefore was washed away from the hexabrom compound with this solvent. The separation thus roughly effected was completed by crystallisation from petroleum ether, in which the hexabrom compound is less soluble. In this way the constant melting-point 115° (uncorr.) was at last obtained. The analyses given in the introduction show this is the *pentabromodiacylmonoethylhemiacetal*.

Properties.—It crystallises from petroleum ether in short broad prisms terminated by a second prism at right angles to the first, so that they look like somewhat lengthened octahedra. They are modified by many small planes. It melts at 115° (uncorr.), and is soluble in alcohol, methyl alcohol, benzene, tetrachloride of carbon, or glacial acetic acid; insoluble in water. Sodium hydroxide did not set free bromoform from it.

The following experiments to obtain the corresponding methyl compound gave negative results:—Hexabromodiacyl with methyl alcohol and acetone, its monomethylhemiacetal with acetone, or with methyl alcohol and acetone. The only substance isolated in each case was hexabromodiacylmonomethylhemiacetal.

Action of Potassium Iodide on Hexabromodiacyl.—To a solution of 3 grms. of potassium iodide in 25 cc. of water was added 1 grm. of powdered hexabromodiacyl. A brown colour soon appeared, which gradually grew darker, and was accompanied by the evolution of carbonic dioxide in large quantity. After two days a crystalline precipitate had formed, which was filtered out, washed with a solution of potassium iodide to remove the free iodine, and allowed to stand on a porous plate for ten to twelve hours, at the end of which time the iodine had disappeared to judge from the colour. It was not easy to find a good solvent for this substance, as most of the common ones set free iodine from it, but at last it was found that tetrachloride of carbon gave good crystals without a coloured mother-liquor, and accordingly it was crystallised five times from that, when it decomposed between 122° and 125° ; but this point varied so much with the conditions of the heating that it is of little value as a criterion of purity. We therefore analysed specimens from the first, second, third, and fourth crystallisations, and found that the impurities had been removed by the first, as the results from the last three (given below) agreed with each other.

Subs., 0.1468, 0.2129, 0.1366, 0.1845, 0.2439; AgBr, 3.461, 0.2568, 0.3730, 0.2392; CO_2 , 0.0519, 0.0679; H_2O , 0.0122, 0.0133. Found—BrI₃, 90.28, 90.44, 90.40; C, 7.67, 7.59; H, 0.78, 0.61.

The formula we assign to this substance is $\text{C}_3\text{H}_2\text{BrI}_3\text{O}$, which requires BrI₃, 89.52; C, 6.99; H, 0.39; molecular weight, 515 (found 475, 485, 502). These percentages do not agree very well with those found, but this is accounted for by the fact that the only solvent which did not decompose our substance was tetrachloride of carbon, and according to our experience substances crystallised from this usually give poor results on analysis. If this empirical formula is correct the substance is probably triiodobromoacetone, and we have adopted this structure for it provisionally.

Properties of Triiodobromoacetone?—It crystallises from tetrachloride of carbon in slender lemon-yellow needles, which turn brown in the light. It melts with decomposition at 122 – 125° , but this point is decidedly indefinite. It is soluble in alcohol, methyl alcohol, benzene, chloroform, or tetrachloride of carbon; essentially insoluble in petroleum ether. All of these solvents decompose it somewhat with liberation of iodine, but this action at least with tetrachloride of carbon, which is therefore the best solvent for it. Fuming nitric in the cold or strong nitric acid when heated decomposes it, setting free iodine.

Nitric acid diluted with acetic acid had no action in the cold, but on warming iodine was set free. Ammonium hydroxide gave a smell like iodoform, and ammonium iodide was found in the liquid. Sodium hydroxide also gave iodoform, to judge by the smell. Hydric dioxide did not act on it.

Hexabromodiacylmonoethylhemiacetal was not affected by potassium iodide solution even at 100° .

ON MAGNETIC OXIDE OF CHROMIUM.

By TAKE SONE and TORAJIRO ISHIWARA.

1. FROM the theoretical point of view it is a very interesting and important fact that non-magnetic elements constitute a compound or an alloy having the ferromagnetic property. The most remarkable example is the alloy discovered by Fr. Heusler, 1903 (*Verh. d. Deutsch. Phys. Gesellsch.*, 1903, v., 219; *Marburger Schriften*, 1905, vii., 98). The same is also observed, though in a much less degree, in some manganese compounds (R. S. Williams, *Zeit. Anorg. Chem.*, 1907, lv., 1; K. Honda, *Ann. d. Phys.*, 1910, xxxii., 1017) or compounds of chromium and oxygen, &c. It was first observed by Fr. Wöhler (*Lieb. Ann.* 1859, cii., 117) that the black oxide of chromium, Cr_5O_9 , which was derived from the chromyl chloride vapour, is strongly magnetic. A. Geuther (*Lieb. Ann.*, 1861, cxviii., 62) repeated Wöhler's experiment and found that the magnetic oxide, $\text{Cr}_5\text{O}_9(2\text{Cr}_2\text{O}_3.\text{CrO}_3)$, is also formed by carefully heating the chromium trioxide, CrO_3 . J. Shukow (*Comptes Rendus*, 1908, cxlvi., 1396) investigated the magnetic properties of chromium trioxide and found that in order to obtain the magnetic oxide from the chromium trioxide the compound must be kept at a constant temperature between 500 and 510°C . He also found that the compound thus obtained had the greatest susceptibility ($\chi=6.8 \times 10^{-3}$) and corresponded to the formula Cr_4O_9 . Recently Prof. K. Honda and one of us (K. Honda and T. Soné, *Sci. Rep.*, 1914, iii., 223) took up the same problem and determined the magnetic susceptibilities of oxides of chromium formed by continuously heating the chromium trioxide in the atmosphere. The result was that the specimen having the greatest susceptibility was obtained by heating the chromium trioxide at a temperature of 445°C ., and that it was perhaps a mixture of three compounds— Cr_6O_{15} , Cr_5O_9 , and Cr_2O_3 . In the present experiment we started from chromyl chloride, CrO_2Cl_2 , as Fr. Wöhler and A. Geuther did, and examined the magnetic properties of the specimen obtained by heating it to certain temperatures.

2. The process of obtaining the magnetic compound from chromyl chloride was as follows:—A quantity of liquid chromyl chloride was introduced into a retort to whose neck a long tube, made of hard glass about one metre long, was fused.

The tube was horizontally placed in a combustion furnace and gently heated uniformly along its whole length by a series of burners, and was kept at a temperature of about 400°C . The bulb of the retort was then heated and the vapour which escaped from it was passed through the tube for about five hours. The vapour then condensed in the inner wall of the tube and formed a grey or black coating inside the tube. The colour of the coating, which was formed in the upper half of the tube, was generally grey and that in the lower half was generally black. We treated the grey and black deposits separately in our experiments.

The tube was cut into several small pieces, each being about 10 cm. long, from each of which the coating of the compound was removed and ground into fine powder. The powder was then put into a thin glass tube, 3 mm. in its internal diameter and 10 cm. long, one of its ends being closed, and pressed as compactly as possible. In this form the specimen was subjected to our magnetic experiment.

3. For investigating the magnetic properties of the compound the magnetometric method was used. The arrangement was the same as that used by Prof. K. Honda (*Sci. Rep.*, 1913, ii., 60) in the experiment for investigating the magnetic properties of iron and steel, so that we may here omit its description. As the magnetisation of the compound was considerably small compared with that of iron and steel the compensation of the effect of magnetising coil on the magnetometer was carefully made.

Some results of our experiment at an ordinary temperature are given in Table I. The numbers No. 1, 2, &c., refer to the specimens taken from different portions of the tube; thus specimen No. 1 is the one taken from the farthest portion of the tube from the retort, No. 2 the one taken from the next portion of the tube, and so on. The residual magnetism was also observed and included in the table.

TABLE I.

No. 2.—Grey.			No. 2.—Black.		
H.	I.	Ir.	H.	I.	Ir.
50.96	3.168	0.45	50.96	1.352	0.0
100.9	5.302	0.65	100.3	2.422	0.17
146.0	7.242	1.03	153.9	4.000	0.45
270.7	11.32	1.49	267.0	6.309	0.90
370.0	13.00	1.68	366.8	8.449	0.67

No. 3.—Grey.			No. 3.—Black.		
H.	I.	Ir.	H.	I.	Ir.
48.83	4.033	0.54	52.55	3.277	0.26
98.20	7.959	0.75	106.7	6.668	0.94
150.2	11.19	1.34	145.4	9.343	1.32
222.4	14.90	1.72	230.4	14.07	2.00
287.7	18.12	2.15	297.3	15.97	2.26
359.9	20.60	2.47	363.1	18.08	2.26

No. 5.—Black.			No. 6.—Black.		
H.	I.	Ir.	H.	I.	Ir.
51.49	2.549	0.28	51.49	2.715	0.0
109.9	5.381	0.92	106.2	5.002	0.57
170.9	8.425	1.56	143.9	6.860	1.00
217.6	8.133	1.56	210.7	9.361	1.00
314.2	14.73	2.05	264.9	11.22	1.29
			362.5	13.86	1.43

In Table I., H denotes the magnetising, external field, I the intensity of magnetisation, and Ir the residual magnetism.

The intensities of magnetisation of the six specimens slightly differ from each other, the largest being 20 in a field of 360 gauss for specimen No. 3, while the smallest value is 8 in the same field for specimen No. 2. The intensities of magnetisation of the remaining four lie between these limits. The susceptibilities of the specimens slightly decrease with the increase of the field. For a field of 200 gauss the values of susceptibility range from $\chi = 7.0 \times 10^{-2}$ to $\chi = 2.5 \times 10^{-2}$. The values are about ten times as large as those obtained by J. Shukow (*loc. cit.*). The specimens affect an ordinary compass-needle moderately.

4. To determine the composition of the specimens, the three of them, No. 3 (black), No. 6 (black), and No. 2 (black) were taken. Each specimen, in a double porcelain crucible, was heated to about 1000° C. for about forty minutes in an electric furnace. The mass of the specimen before and after heating was measured. As the final product should be chromic oxide, Cr_2O_3 (K. Honda and T. Soné, *loc. cit.*), we can calculate the composition of the specimen by supposing it to be composed of the two compounds Cr_2O_3 and Cr_2O_3 before heating. The mass before and after heating and the results of calculation are given in Table II.

Thus we may conclude that the strongly magnetic specimen No. 3 (black) is chiefly composed of the magnetic compound Cr_2O_3 .

To determine the critical temperature of the compound specimens No. 3 (black) and No. 5 (grey) were used. The

method of investigation was exactly the same as that followed by Prof. K. Honda (*loc. cit.*) in the experiment above cited. The two specimens gave an almost identical result. The critical temperature was found to be about 150° C., and the magnetic transformations by heating and cooling took place almost reversibly. The above value for the critical point is about 30° higher compared with that obtained by J. Shukow (*loc. cit.*).

TABLE II.

Specimen.	Mass.		Percentage.	
	Initial. Grm.	Final. Grm.	Cr_2O_3 . Per cent.	Cr_2O_3 . Per cent.
No. 3.—Black..	1.1498	1.0843	96.0	4.0
No. 6.—Black..	0.6229	0.5895	90.3	9.7
No. 2.—Black..	0.7925	0.7693	49.3	50.7

In conclusion we express our cordial thanks to Prof. K. Honda, under whose direction the present experiment was conducted.—*Science Reports, Tohoku Imperial University, Japan*, iii., No. 6.

ON A GALLIUM-INDIUM ALLOY.

By PHILIP E. BROWNING and HORACE S. UHLER

A FEW months ago Mr. F. G. McCutcheon, chemist of the Bartlesville Zinc Company, observed some mercury-like globules upon the surface of a leady residue from the distillation of zinc. The appearance of these globules seemed to be due to the fact that the residue had been stored away in a warm place, and the phenomenon suggested to the observer the subjection of the residue to a sweating process. This treatment resulted in a more abundant separation of the peculiar material, which, from the character of its source and its low melting-point, suggested the element gallium. It proved to be essentially an alloy of that element with indium (Hillebrand and Scherrer, *Journ. Ind. and Eng. Chem.*, viii., 225; this article appeared after our paper had gone to press.—Authors).

Through the kindness of the manager (Mr. K. Stock) and the chemist of the company we have been supplied with several grms. of the alloy and a considerable amount of the leady residue. Rough analyses of these products show the gallium-indium alloy to contain about 10 per cent of indium with small amounts of zinc and lead and spectrographic traces of copper and silver. The leady residue contains about 95.6 per cent of lead, a fraction of 1 per cent of copper, about 3 per cent of gallium and indium together, and about 1.2 per cent of zinc.

The alloy is not very vigorously attacked by the common acids, especially by nitric acid, nor by potassium or sodium hydroxide, although all of these reagents act upon it more or less, especially upon warming. Aqua regia dissolves it very readily. From a solution of the alloy the hydroxides of gallium and indium may be precipitated together by ammonium hydroxide in the presence of ammonium chloride, a method of separation from zinc first worked out by Lecoq de Boisbaudran (*Comptes Rendus*, xciv., 1628).

Other procedures suggested by him are the separation of gallium from indium by treating a solution containing them with potassium or sodium hydroxide in excess, which dissolves the gallium hydroxide (*Comptes Rendus*, xciv., 410), a method followed by us with fair success, and the separation from aluminium, chromium, and beryllium, elements which form a group with gallium because their hydroxides are not only precipitated by ammonium hydroxide in the presence of ammonium chloride but are soluble in sodium or potassium hydroxide, the separation being accomplished by making the alkaline

solution of the hydroxides strongly acid with hydrochloric acid and precipitating as the ferrocyanide (*Comptes Rendus*, xciv., 1228, 1439).

Gallium may be precipitated electrolytically by passing a current through an alkaline solution containing the element (Schucht, *Chem. Zeit.*, 1880, 292; Erlich, *Ibid.*, 1885, 78; Küner, *Ibid.*, 1885, 1826). By this method gallium may be separated from indium, as our experiments have shown, practically no spectrographic evidence of indium being found in the product.

A fractional crystallisation of the ammonium-gallium and the ammonium-indium alums has resulted after six crystallisations in a marked separation, the ammonium-gallium at the less soluble end of the series giving no flame-test for indium, while the ammonium-indium alum at the more soluble end gave abundant evidence of indium in the flame. This method will be studied more in detail with the substitution of other alkalis for ammonium. The fact that gallium and indium are alum-forming elements makes this method promising for the removal of the non-alum-forming elements which may be associated with them, and this possibility also will be further investigated.

The results obtained by purely physical processes will now be presented. Since no data on the boiling-point of gallium could be found the following experiments were performed. A transparent silica tube, of internal diameter 0.7 cm. and about 30 cm. long, was first sealed off round at one end by fusion in an oxygen-illuminating gas flame. After introducing about 0.4 cc. of the alloy the tube was joined by sealing-wax to a long glass tube which led to a Gaede rotary mercury pump. The fused end of the tube where the alloy was situated was heated red-hot for three hours with an ordinary blast flame while the pump was kept in action and the sealing-wax was cooled by running water. The silica tube was nearly horizontal and the pressure in the glass tube was less than 0.0005 mm. This process removed all the zinc and other elements of relatively low boiling-points but the gallium-indium alloy showed no signs of boiling. A bulb made from a silica test-tube was then fused to the end of a new quartz tube and the liquid globule which had not distilled in the previous heating was dropped into the bulb. While the pump and ordinary blast flame were kept going the bulb was also heated very cautiously with an oxygen-illuminating gas flame. The alloy then disintegrated with violence, shooting very fine particles of the liquid and a grey powder for a distance of 15 cm. along the axis of the tube. Even when the silica bulb was dazzling white and began to cave in there remained a globule of metal which did not appear to diminish in mass on continued intense local heating. This globule was subsequently burned in the carbon arc and the spectrogram showed that it was nearly pure gallium. As might be expected from the tabulated boiling-points (at 76 cm. pressure) most of the copper (b.p. 2310° C.) had not been driven off. Not a trace of lead (b.p. 1525° C.) could be detected. The amount of indium remaining was very small. It seems safe to conclude that the boiling-point *in vacuo* of pure gallium is greater than 1600° C. and that prolonged heating in a suitable furnace at a temperature of about 1800° C. would effect a complete separation of indium from the alloy.

The density of the specimen was found to be 5.91 grms. per cc. at 20° C., the value given in the standard tables being 5.95. The smaller value cannot be accounted for on the ground of contamination with silicon from the walls of the tube because this hypothesis is not consistent with the spectroscopic evidence. The melting-point of the globule was not absolutely sharp, but the metal consistently fell through a platinum ring, of smaller diameter than the solid disc, at a temperature of 29.5° C. As recorded by other observers the metal remained liquid at 0° C. and showed no signs of congealing at the expiration of several hours. It may be of interest to note that when on different occasions small globules of the fairly pure metal and very impure alloy were partially volatilised in

the electric arc there usually remained on the positive carbon a greyish white vitreous mass having a definite crystalline structure.

Notwithstanding the fact that a thorough investigation of the spectroscopic properties of gallium is now in progress it may not be premature to record the results already obtained in the process of general orientation. The alloy was volatilised in a direct current arc (110 volt mains) with regraphitised Acheson graphite electrodes. The spectrograph contains an excellent concave grating (by Anderson) of one metre radius of curvature and is an improved form of the instrument designed and made by one of us in the year 1904 (see "Atlas of Absorption Spectra," by H. S. Uhler and R. W. Wood, Carnegie Institution of Washington, Publication No. 71, May, 1907). The dispersion is such that 1 mm. includes on the average 25.25 Å in the first order. Since the camera covers the interval from 2000 Å to 7600 Å the identification of ultra-violet lines is facilitated by the superposition on the first order of the second and third orders. The films used were made to order through the kindness of Dr. C. E. K. Mees, and they are easily sensitive from 2000 Å to 7500 Å. The wave-lengths given below are highly tentative. The first negative of the alloy (taken January 22, 1916) brought out the following facts, which have been subsequently verified by numerous exposures with much purer material in the crater of the arc. There is a new band spectrum due either to gallium or to gallium oxide (but very probably due to the gallium molecule) the wave-lengths of the heads of which are roughly 3889, 3778, 3677, 3586 (?), 3495, and 3415. The head near 3586 is partially concealed by the 3590 band usually ascribed to cyanogen. The band commencing at 3889 is by far the strongest and has a very sharp, well-defined edge. The intensity of the successive bands decreases as the wave-length becomes smaller. Moreover the heads of the fainter bands are not sharp, but this may be due to under-exposure. On the other hand the individual bands shade off toward the red. The dispersion and resolving power are so low that there seems to be no separation of the bands into fine lines. These bands extend a relatively long distance and appear at first glance to form a continuous background to the entire region from 3415 to 4000. The cyanogen bands, on the contrary, show fine line structure even in the first order.

A series of eleven lines occurs between 3890 and 4030. These lines are comparatively fine and close together, and separate more and more as the frequency increases. The group probably constitutes the heads of a set of fine bands, which are narrow and shade off toward the less refrangible side. Various careful tests show that indium is not responsible for the production of any of the bands mentioned above. Both sets of bands seem to be best developed when the gallium is first heated in the arc and the metallic vapour is evolved copiously.

In addition to the lines recorded by earlier investigators, the negatives of the purest specimens of gallium which we have so far been able to produce contain lines at λ 2259, 2294, 2338, 2371, and 2418. These lines have the character of the heretofore known gallium lines and they certainly do not pertain to any of the impurities, such as copper, indium, lead, silver, tin, zinc, &c. An attempt to discover a hypothetical ultra-violet absorption spectrum of the vapour of gallium failed. It is highly probable that this negative result was due to the fact that it was not feasible to heat the large silica bulb used to a higher temperature than was produced by the flame of a Meker burner. As soon as possible the wave-lengths of the gallium lines will be accurately determined by means of a 21 ft. grating, so that the constants of the series formula may be calculated independently of the analogous data for aluminium, thallium, indium, &c.

The authors wish to make acknowledgment to Dr. W. F. Hillebrand, of the Bureau of Standards, who first called their attention to the existence of this alloy.—*American Journal of Science*, xli., 351.

"RELATIVE STABILITIES" IN POLLUTED WATERS CARRYING COLLOIDS.*

By ARTHUR LEDERER,
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As a rule, all river waters contain more or less colloidal matter in the form of very finely-divided silt. Polluted waters also carry colloids of sewage origin mainly derived from the faecal matter.

Only recently has the importance of colloids been recognised in sewage disposal and water purification. We know that the colloidal matter in sewage affects the putrescibility of the liquid more than the heavier coarse suspended matter. The removal of the colloids by simple filtration—not biologic filtration—results in an improvement which is, however, much less than the one effected by biologic treatment but far more than by settling (Lederer, *Am. Journ. Pub. Health*, Feb., 1912). The study of colloids has given the science of chemistry a new aspect. Colloidal chemistry has explained some phenomena in nature as well as technology, heretofore not clearly understood. We differentiate between crystalloidal and colloidal state of matter. A very large number of inorganic substances, heretofore known only in the crystalloidal state, have been prepared in the colloidal. Some substances, such as proteins, starch, gum, and glue, are known in the colloidal form only. Suspensions of colloidal clay remain suspended in the water for days and weeks. The addition of electrolytes, such as common salt, sodium sulphate, calcium sulphate, or sodium nitrate, accelerates sedimentation. The reason for this is (1) the electrostatic attraction between the colloids and the ions carrying the opposite electrical charge; (2) the removal of the water of the colloid. Hygroscopic electrolytes are therefore particularly efficient. Colloidal clay adsorbs aniline dyes such as methylene blue. By adsorption we understand the concentration of a dissolved salt on a surface due to difference in surface tension or electric potential. Clays also adsorb and retain other substances such as oils, fats, starch, proteins, certain inorganic dyes, all aniline and plant colouring matter, urine and faecal matter, putrid odours, and a large number of other substances. This property of adsorption has led Prof. Rohland, of Germany, to develop his clay treatment of sewage and industrial waste waters. Adsorption is selective. An interesting study on this point has been made by Parker (*Journ. Ind. Eng. Chem.*, 1914, p. 831).

When applying methylene blue to waters carrying colloidal suspensions of clay, the dye is adsorbed by the clay, and sedimentation occurs, leaving the liquid colourless. The sediment is blue. This adsorption may be only partial; it may take place quickly or slowly, all depending upon the quantity and the character of the colloidal matter present. The adsorption interferes seriously with the quantitative determination desired on the degree of putrescibility of the liquid. In other words, "relative stabilities" obtained in such waters by the methylene blue method cannot be correct. Spitt and Weldert in their original communication ("Mitt. kgl. Prüfungsanst., *Wasserversorgung*, Heft 6, p. 160) advise the observation of decolorisation of the sediment after adsorption takes place, though their observations are more of a qualitative nature, and in such cases the exact time element is of less importance. In obtaining Phelps' "relative stabilities," the time element is all-important.

Until recently the writer disregarded the decolorisation of the liquid in polluted river waters, and accepted the decolorisation of the sediment as the criterion. Correspondence between the writer and Dr. F. E. Hale, of the Mount Prospect Laboratory, Brooklyn, N.Y., developed a difference of opinion regarding the reliability of this procedure. Dr. Hale held that the methylene blue once

thrown out of solution is probably inert, and that therefore the decolorisation of the liquid should be accepted as the sole index of the putrescibility. Dr. Hale's procedure consists in adding 1 cc. of methylene green solution at the beginning, and continuously thereafter as demanded by adsorption until a slight colour persists in the liquid. Decolorisation of this was taken as the end-point. Dr. Hale considers that this method gives good relative results, but probably does not represent absolute values. My aim was to obtain correct relative stabilities, while Dr. Hale's procedure aimed at relative results. In this respect our problem differed. Notwithstanding, I decided to investigate whether the observation of the decolorisation of the sediment actually furnishes correct relative stabilities, and if not, which procedure would have to be followed. Jackson and Horton (*Journ. Ind. Eng. Chem.*, June, 1909, vol. i.) recommend the use of as little methylene blue as possible, on account of its antiseptic properties, and the writer (Lederer, *Am. Journ. Pub. Health*, iv., 241) in investigating the quantities recommended in the "Standard Methods" fixed the amount as 0.4 cc. of a 0.05 per cent aqueous solution per 150 cc. bottle capacity. When working with waters carrying colloids it is clear, of course, that there should always be 0.4 cc. or less of the colouring matter in solution, provided the sediment containing the precipitated colouring matter is actually inert. An excess of colouring matter in solution would interfere with obtaining correct results. If the colouring matter in the sediment retains its antiseptic qualities, even though to a lesser degree, it would still be impossible to obtain correct figures. The entire question depends, of course, upon the value of all methylene blue or other similar "relative stabilities" when applied to liquids other than sprinkling filter effluents.

Since the decolorisation of the blue colour coincides fairly closely with the elimination of the total available oxygen, I first determined the oxygen at the time of decolorisation of the liquid and sediment as well. An artificial turbidity of 100 was imparted to a putrescible sewage-water mixture, and a number of glass stoppered bottles were filled with this liquid. A number of these bottles were coloured in the proper proportion with methylene blue, the others remained as "blanks" for the determination of the residual available oxygen. The results are given in Table I.

These tabulated results indicate the following conclusions:—A very serious mistake can be made by assuming that the decolorisation of the sediment in silt-bearing waters is the correct measure of the "relative stability." Experiments 3, 4, 5, 6, and 7 show that the decolorisation lags far behind the elimination of the available oxygen in such liquids, or, in other words, the methylene blue once adsorbed is largely inert as an indicator. This bears out Dr. Hale's assumption. The adsorbed liquid is, however, not entirely inert, as otherwise the sediment would never decolorise. The fact that the sediment decolorises only under prolonged ultra-anaerobic conditions makes such an observation useless for quantitative purposes. Reliance on the decolorisation of the liquid is equally doubtful because we cannot tell to what extent the decolorisation is really adsorption. We can only be fairly certain of obtaining accurate "relative stabilities" if we knew that 0.4 cc. or less of the colouring matter per 150 cc. bottle capacity would remain in excess over the adsorption requirements, and that the adsorbed methylene blue was entirely inert. This cannot be ensured under practical conditions, but remains a matter of chance. If more than 0.4 cc. of the colouring matter remains in solution the antiseptic qualities of the dye would make itself felt and higher "relative stabilities" would result. The adsorption of the colouring matter seems to bear a definite relation to the amount of colloidal matter present, and indeed some German observers have recommended a quantitative procedure for determining colloids on this basis. The methylene blue tests in waters carrying colloids is therefore of negative value only; i.e.,

* Read before the Laboratory Section American Public Health Association, Jacksonville, Fla. From the *Chemical Engineer*, xxii, No. 4.

TABLE I.—*Elimination of available Oxygen in Turbid Waters on applying the Methylene Blue Putrescibility Test.*

Serial No.	Date and time, 1914.	No. of cc. 0.05 p.c. methylene blue added per 150 cc. capacity.	Colour of supernatant liquid in 24 hours.	Time of decolorisation of liquid in hours.	Time of decolorisation of sediment in hours.	P.P.M. total initial available oxygen.	P.P.M. residual oxygen at time of decolorisation of liquid.
1.	April 14, 11 a.m.	0.4	Colourless	24	Sediment	23.3	10.5
		0.8	"	24	did not	23.3	10.5
		1.2	"	24	decolorise in	23.3	—
		2.0	Blue	Blue after ten days	ten days	23.3	—
2.	April 15, 10.30 a.m.	0.4	Colourless	24	Sediment	23.5	8.8
		0.8	"	24	did not	23.5	8.8
		1.2	"	24	decolorise in	23.5	8.8
		2.0	Blue	Blue after ten days	ten days	23.5	—
3.	April 20, 11 a.m.	0.4	Colourless	20 (a)	88	20.1	0.5
		0.8	"	20 (a)	105	20.1	0.5
		1.2	"	20 (a)	112	20.1	0.5
		2.0	Slightly blue	45	119	20.1	0.4
4.	April 23, 11 a.m.	0.4	Colourless	24	Sediment	22.1	4.7
		0.8	"	24	did not	22.1	4.7
		1.2	Slightly blue	48	decolorise in	22.1	0.6
		2.0	blue	93	ten days	22.1	0.5
5.	April 27, 11 a.m.	0.4	Colourless	20 (a)	52	18.7	0.5
		0.8	"	20 (a)	61	18.7	0.5
		1.2	"	20 (a)	70	18.7	0.5
		2.0	Blue	45	76	18.7	0.4
6.	April 29, 11 a.m.	0.4	Colourless	20	100	21.0	2.9
		0.8	"	20	118	21.0	2.9
		1.2	"	20	127	21.0	2.9
		2.0	Blue	45	142	21.0	0.7

(a) Decolorised during the night, therefore estimated but roughly. The absence of the residual oxygen at the time of the decolorisation of the liquid is of course due to the fact that the oxygen has not been determined at the exact time of decolorisation.

if the blue colour of the liquid persists irrespective of adsorption, the "relative stability" is 100, or an excess of oxygen may be present.

A number of coagulants, such as freshly precipitated aluminium hydrate, magnesium hydrate, calcium carbonate, and calcium oxide, were employed to mechanically settle the colloids previous to introducing the colouring matter. The results were not sufficiently encouraging to follow this line of experiment. The addition of electrolytes to sewage, such as common salt, did not accelerate the sedimentation sufficiently to be of practical advantage.

I am forced to conclude that it is useless to determine "relative stabilities" in turbid waters by the methylene blue method. This is unfortunate, since it robs us of a simple and convenient field procedure. To obtain the correct oxygen demand in such waters, the following procedure is requisite:—

Determining the Initial Available Oxygen.—The free oxygen has to be determined on the spot. A sample for nitrite and nitrate determination can be preserved with chloroform and shipped to the laboratory. Three other samples should be collected carefully to avoid aeration. To one sample add either a certain quantity of fresh water (free of nitrites and nitrates) with a known oxygen content or a definite quantity of saltpetre (Lederer, *Journ. Infect. Dis.*, xiv., 482). Personally, I prefer to add saltpetre, since it is a much simpler procedure. The other two samples remain as originally collected. All of these samples are now incubated in closed bottles for ten days at 20° C. At the end of this incubation period the residual available oxygen is determined in the samples devoid of saltpetre or additional water. The other sample is examined quantitatively for nitrites and nitrates. If free oxygen remains at the end of incubation the residual saltpetre oxygen need not be determined. All figures are referred to 1 litre of original river water. The nitrite nitrogen multiplied by 1.7 and the nitrate nitrogen multiplied by 2.9 express equivalents of oxygen. The initial available oxygen minus the residual oxygen expresses the biochemical oxygen demand. When the water is very

badly polluted, the free oxygen sample need not be incubated for the reason that the free oxygen is certain to be absent after incubation. In connection with these incubations, it is important to keep in mind that the nitrites and nitrates are attacked while free oxygen is still present. As a rule, the nitrites and nitrates begin to be attacked when the free oxygen content is reduced by about 50 per cent.

THE PHOSPHORIC ACID IN STARCH.

By JOHN H. NORTHROP and J. M. NELSON.

UP to the present time no definite evidence has been brought forth as to whether the phosphoric acid present in starch is in chemical combination or not. Ford (*Journ. Soc. Chem. Ind.*, 1904, xxiii., 414), Fernbach (*Comptes Rendus*, 1904, cxxxviii., 428; 1912, clv., 617), Fernbach and Wolff (*Ibid.*, 1905, cxl., 1403), Malfitano (*Ibid.*, 1906, cxliii., 400), Malfitano and Moschkoff (*Ibid.*, 1910, cl., 711), Fouard (*Ibid.*, 1907, cxliv., 501; 1908, cxlvi., 285), Thomas (*Biochem. Bull.*, 1914, iii., 407), Grewzewska (*Comptes Rendus*, 1911, clii., 785), and others, employing a variety of methods, such as precipitation with alcohol, acetone, freezing or dialysis, &c., all were unable to completely free the starch from its accompanying phosphorus.

Samec (*Kolloidchem. Beihefte*, 1911, iii., 123; 1912, iv., 133; 1913, v., 141; 1914, vi., 23) seems to have shown quite conclusively that the starch granules are not homogeneous and that the phosphorus is associated with the exterior of the grains (amylopectin). He further states that the phosphoric acid and the amylopectin are chemically combined in the form of an amylophosphoric acid, since the only way to account for the decrease in viscosity and cataphoresis, and increase in solubility, osmotic pressure, and activity, when starch solutions are heated or allowed to stand, is by the hydrolysis, with the liberation of free phosphoric acid from a compound of this type. Samec measured what he considered to be the hydrolysis

of the amylophosphoric acid by the increase in the conductivity of the solution. Results obtained independently in the laboratory of the Columbia University, however, show that little or no free phosphoric acid is liberated under those conditions, and that therefore the change in properties of a starch solution under these conditions cannot be attributed to the hydrolysis of such an amylophosphoric acid. It was found, on the contrary, that several hours' heating with 10 per cent acid were necessary for the liberation of all the phosphoric as free phosphoric acid. This is in keeping with the behaviour of other phosphoric acid esters studied by Fisher (*Ber.*, 1914, xlvii., 3193), Anderson (*Journ. Biol. Chem.*, 1915, xx., 487), Plimmer (*Biochem. Journ.*, 1913, vii., 43), and Levene and Jacobs (*Ber.*, 1908, xli., 1905).

The results of the present investigation show:—

First. The phosphorus is chemically combined in the starch grains and cannot be removed by extraction with dilute acid either in the form of free phosphoric acid or in combination. This shows that its presence cannot be due to contamination with other material present in the potatoes from which the starch used in this investigation was obtained.

Second. A method has been found for the isolation from partially hydrolysed starch of a compound of relatively high phosphorus content, of definite composition and containing a carbohydrate.

Third. This compound differs from Samec's hypothetical amylophosphoric acid in that it is more stable towards hydrolysis.

Fourth. The possibility that the compound is derived from proteins in the starch is shown to be very remote, in view of the small amount of nitrogen present in the original starch and of the fact that acetyl derivatives were obtained that contained phosphorus but no nitrogen.

Experimental.

Determination of Phosphorus.—The sample was decomposed by the Neumann method and the phosphorus precipitated as ammonium phosphomolybdate (Hibbard, *Journ. Ind. Eng. Chem.*, 1913, v., 998) and determined by titration with alkali (Falk and Sugiura, *Journ. Am. Chem. Soc.*, 1905, xxxvii., 1507), formaldehyde being added to remove the ammonia (Bang, *Biochem. Zeit.*, 1911, xxxii., 443). The starch used in this investigation was potato flour and was found to contain 0.06 per cent phosphorus by this method.

No phosphate could be extracted by dilute acid, while a known amount of phosphate added to the starch before extraction could be completely recovered, showing that the phosphorus is not present as an adsorbed impurity.

Ten grms. of starch were stirred twenty-four hours with 500 cc. of 2 per cent hydrochloric acid, filtered, the filtrate evaporated to 150 cc., and the phosphorus precipitated with molybdate as usual. The amount of precipitate was too small to determine. The experiment was repeated with the addition of 0.0064 gm. of phosphorus as secondary potassium phosphate to the solution before extraction, and resulted in the recovery of 0.00638 gm. of phosphorus.

Determination of Nitrogen.—Various figures are given in the literature for the percentage of nitrogen present in potato starch. König ("Nahrungs und Genussmittel," 3rd ed., I., 626) gives 0.1 per cent, Fernbach (*loc. cit.*) found 0.018—0.038 per cent, and Samec (*loc. cit.*) reports a trace. Analysis of 5 grms. of the starch used in this investigation gave negative results by the Kjeldahl method. The Dumas method, using a 1 gm. sample, also gave negative results. A slight coloration was obtained in the nitroprusside test, which was found to be less than that obtained from a mixture of crystallised egg albumin and cane sugar containing 0.1 per cent nitrogen.

Isolation of a Compound of Higher Phosphorus Content.—Born and Nelson (*Journ. Am. Chem. Soc.*, 1913, xxxvi., 393) have shown that the phosphorus-bearing polysaccharide or invertase undergoes acetolysis in such a way

as to increase the percentage of phosphorus. Acetylation of starch, however, led only to the isolation of products containing 0.06—0.13 per cent phosphorus. Since no products containing a higher percentage of phosphorus could be isolated by this method it was abandoned. The acetyl derivatives were free from nitrogen, so that it seems improbable that the phosphorus was of protein origin.

Acid Hydrolysis.—It was found, however, that starch could be partially hydrolysed by acid without splitting off more than a small percentage of the total phosphorus and that compounds of relatively high phosphorus content could be isolated from this partially hydrolysed starch solution.

Ten grms. of starch were dissolved in 100 cc. of 10 per cent hydrochloric acid and the solution heated on the water-bath until no precipitate was obtained on adding a drop of the solution to alcohol. The solution was then filtered from the precipitate of retrograded starch, which always formed, and the amount of free phosphoric acid determined in the filtrate by precipitation, first with magnesia mixture and then with molybdate. The experiment was then repeated with the addition of a known amount of a solution of secondary potassium phosphate to the solution before hydrolysis. The results obtained by difference in this way were the same as those obtained directly, showing that this phosphorus was not retained by adsorption. Only 3—5 per cent of the total phosphorus could be found in the solution as free phosphoric acid when the starch was hydrolysed under these conditions. The results of four such determinations are given in Table I.

TABLE I.

Grms. starch.	10.	10.	10.	10.
Grms. P found ..	0.00023	0.00024	0.00662	0.00664
Grms. P added ..	—	—	0.0064	0.0064
P from starch ..	0.00023	0.00024	0.00022	0.00024
P.c. P hydrolysed	3.83	4.00	3.66	4.00

These results render it improbable that the increase in conductivity noticed by Samec, when starch solutions were heated or allowed to stand, was due to the liberation of free phosphoric acid.

Long-continued hydrolysis with acid resulted in the liberation of all the phosphorus as free phosphoric acid. Thus it will be noticed that the starch compound differs from phytin in this respect, since Anderson and others have shown that phytin is completely hydrolysed only by heating with strong acid under pressure (Anderson, *Journ. Biol. Chem.*, 1915, xx., 487; Plimmer, *Biochem. Journ.*, 1913, vii., 43).

Ten grms. of starch were dissolved in 100 cc. of 10 per cent hydrochloric acid and heated on the water-bath with a reflux condenser for fourteen hours. Found, by precipitation as magnesia ammonium phosphate and then as molybdate, 0.0059 gm. phosphorus, equivalent to 98.3 per cent.

A compound containing the combined phosphorus could be precipitated from the solution by neutralising the acid with barium hydroxide and adding two volumes of alcohol. This precipitate, after removal of the barium with sulphuric acid and subsequent precipitation with alcohol, contained 3—5 per cent phosphorus and was later shown to be an organic phosphoric acid. In order that the material could be obtained in sufficient quantities to work with it was necessary to determine the conditions for its isolation, so that it could be carried out on a large scale.

Conditions for Hydrolysis.—As it was necessary to precipitate with alcohol attempts were made to hydrolyse the starch in as concentrated a solution as possible. A 25 per cent starch solution was found to be the maximum concentration that could be used, since a higher concentration gave too thick a paste. Hydrolysis with strong acid was found to be the best, since dilute acid favours the formation of retrograded starch, a substance that is exceedingly troublesome to filter.

When working with small quantities it was found possible to evaporate the solution after hydrolysis and subse-

quent neutralisation with ammonia, but when large amounts were used a caramel-like substance was formed that was insoluble in alcohol.

(600 grms. of this substance were obtained in this way from 10 kilograms. of starch. It contained 0.24 per cent phosphorus and yielded acetyl derivatives containing 0.06—1.59 per cent phosphorus. They could not be sufficiently purified to warrant further investigation. Acid hydrolysis led to the isolation of a substance containing 3.9 per cent phosphorus and similar in properties to those obtained direct from starch. These results suggest the possibility of the formation of phosphorus-bearing polysaccharides from simpler compounds under these conditions).

The formation of this insoluble substance was obviated by allowing hydrolysis and evaporation to take place together. The following conditions were found to be the most satisfactory for this purpose:—

Ten kilograms. of starch were suspended in forty litres of water and two litres of concentrated hydrochloric acid added. The mixture was stirred and steam under 50 lbs. pressure led in until the stiff paste which first formed had completely liquefied. The solution was then transferred to large evaporating dishes and heated on the water-bath at 65° until no precipitate was formed on the addition of a few drops of the solution to alcohol. It was then neutralised by solid barium hydroxide and the solution filtered from the precipitate of retrograded starch, barium phosphate, and barium carbonate, through large fluted papers. The solution, usually twenty to twenty-five litres in volume, was precipitated with two volumes 85 per cent alcohol in large precipitation jars and allowed to settle overnight. As much of the supernatant liquid as possible was then syphoned off and the remainder filtered with suction. About 60 grms. of a white hygroscopic substance were obtained in this way from each 10 kilograms. of starch.

Sixty kilograms. of starch were treated by this method, yielding about 300 grms. of the barium precipitate. The product was suspended in water and decomposed by a slight excess of sulphuric acid, the solution filtered, and the residue extracted three times with water and filtered with suction. The original filtrate and washings were combined and the excess acid removed by long stirring with lead carbonate, the lead carbonate and sulphate filtered off, and the solution made slightly alkaline with ammonia and saturated with hydrogen sulphide to remove the lead. The filtrate from the lead sulphide was evaporated under 25 mm. pressure to a thin syrup and precipitated by the addition of eight litres of glacial acetic acid. By pouring the acid carefully down the side of the precipitation jar and then stirring slowly a granular precipitate was obtained that could be easily filtered. The precipitate was washed with absolute alcohol and dried in a vacuum desiccator, first over sulphuric acid and then over potassium hydroxide. Yield 110 grms., marked "Acetic acid precipitate." The acetic acid filtrate after evaporation under diminished pressure and subsequent precipitation with alcohol yielded 75 grms. of a slightly yellowish powder that contained 3.4 per cent phosphorus. This substance has not been investigated further.

Acetic Acid Precipitate.—The crude substance when dry was obtained as a dull white, very hygroscopic powder. It was soluble in water, from which solution it could be precipitated by the addition of alcohol, acetone, or acetic acid. Upon analysis it gave 4.9 per cent phosphorus, none of which was present as inorganic phosphates. Qualitative analysis of the ash showed the presence of small quantities of magnesia, sulphates, chlorides, and silica. It contained no nitrogen and did not reduce Fehling's solution.

Acyl Derivatives.—Owing to the insolubility of the substance in organic solvents purification was attempted by means of acylation, in the hope that in this way products of definite chemical constitution could be isolated. Acetylation, however, led to the formation of uncrystal-

lisable syrups. This difficulty was avoided by benzoylating the compound by means of the Schotten-Baumann reaction, but the products were colloidal and could not be crystallised, so that purification could only be accomplished by precipitation from chloroform or acetone solution by means of ligroin, ether, water, &c. Two amorphous substances were obtained in this way that were fairly constant in phosphorus content:—

		Per cent phosphorus.				
Compound A ..		1.02	1.04	0.99	1.08	1.03
" B ..		1.48	1.42	1.40	1.41	

Since the products could not be crystallised and gave varying values for phosphorus after more extended treatment it is difficult to say whether or not they were chemical individuals.

Lead Salt.—Purification was then attempted by means of the lead salt, which it was found could be precipitated from alcohol solutions by means of lead acetate. The compound obtained in this way contained constant amounts of lead and phosphorus when prepared under different conditions, and appeared to be a definite chemical compound. It was free from inorganic phosphates and from metals other than lead. The results of the analyses of five such preparations with the methods used for their isolation are as follows:—

Preparation No.	1.	2.	3.	4.	5.
Per cent lead ..	30.46	30.30	30.53	30.33	30.38
Per cent phosphorus	3.86	3.80	3.78	3.99	3.90

Method of Preparation.

(1) One gm. of the substance was dissolved in 100 cc. of water and precipitated by the addition of 400 cc. of alcohol. The precipitate was then extracted several times with hot 80 per cent alcohol and the combined filtrates precipitated by the addition of lead acetate. A white flocculent precipitate was obtained, which was filtered off, dissolved in dilute acetic acid, and precipitated with alcohol.

(2) Five grms. of the substance were dissolved in 100 cc. of water and a 10 per cent solution of lead nitrate added until no further precipitate was obtained. 100 cc. of alcohol were then added and the solution allowed to stand in the ice-box overnight. The solution was filtered and the filtrate precipitated by the addition of a saturated solution of lead acetate in 80 per cent alcohol. The resulting precipitate was filtered off and reprecipitated from water solution by means of alcohol.

(3 and 4) Twenty grms. of the substance were dissolved in 200 cc. of water, neutralised with lead carbonate, and 9 grms. of lead nitrate added. The solution was allowed to stand in the ice-box or overnight, filtered, and the filtrate precipitated by the addition of 400 cc. of alcohol.

(5) Five grms. of the substance were dissolved in 50 cc. of water and 10 per cent silver nitrate solution added until no further precipitate was obtained. The silver chloride was filtered off and the excess silver removed by hydrogen sulphide. The hydrogen sulphide was removed by boiling and the solution neutralised with lead carbonate and treated as described under (3).

All preparations were dried for analysis at 60° in *vacuo* over sulphuric acid. Attempts to determine the percentage of carbon and hydrogen were unsatisfactory, owing to the difficulty experienced in burning the substance.

Free Acid.—The free acid was prepared from the lead salt by removing the lead with hydrogen sulphide and precipitating the resultant solution with alcohol, after evaporation of the solution under diminished pressure. The substance contained a constant amount of phosphorus, as shown by the analyses given below.

The substance as obtained by the above method was a perfectly white amorphous powder. It was extremely hygroscopic, contained no ash other than phosphoric acid, and was free from nitrogen. It reduced Fehling's solu-

tion and on hydrolysis with acid yielded a reducing sugar equivalent to 65 per cent glucose and gave a heavy precipitate of glucosazone.

The substance was optically active. $[\alpha]_{D22}^{20} 108^{\circ} 30'$.

Preparation No. (a)	1.	2.	3.	4.	5.	6.
P.c. phosphorus ..	5'30	5'30	5'56	5'24	5'27	5'33
" carbon (a) ..	35'45	35'20.				
" hydrogen ..	5'84	and 5'93.				

(a) It was necessary to remove the ash and grind it with potassium dichromate and repeat the combustion in order to burn the substance completely.

Hydrolysis and Identification of the Sugar.—One grm. of the material was dissolved in 100 cc. of 10 per cent hydrochloric acid and heated on the water-bath for four hours. A large excess of sodium acetate and 2 grms. of phenylhydrazine were then added and the solution heated for two hours longer. A heavy precipitate formed, which was recrystallised from methyl alcohol and water containing a small amount of pyridine, and identified as glucosazone by means of the melting-point and optical rotation. M. p. 204° (uncorr.).

Two-tenths of a grm. dissolved in 4 grms. of pyridine and 6 grms. of absolute alcohol gave a negative rotation (Neuberg, *Ber.*, 1899, xxxii., 3384) in a 25 mm. tube of 27°.

Quantitative Estimation of the Sugar.—0.3384 grm. of the substance was dissolved in 100 cc. of 10 per cent hydrochloric acid and heated on the water-bath for eight hours. The solution was then made up to 100 cc. and the sugar determined in two aliquots of 25 cc. each by Defren's method (Sherman, "Organic Analysis," 1912):—

Grm. copper oxide ..	..	0.1417	0.1416
Glucose equivalent ..	..	0.0630	0.0629
Per cent glucose ..	..	64.86	64.81

Probable Constitution of the Compound.

The simplest formula that will conform to the above analyses is $C_{17}H_{31}O_{16}(H_2PO_3)$, corresponding to the calculated percentages; carbon, 35.66; hydrogen, 5.77; phosphorus, 5.42. According to the formula the lead salt contains a higher percentage of lead than should be present (26.73 per cent) were the metal combined only with the phosphoric acid. The percentage of phosphorus in the lead salt calculated on a lead-free basis agrees, however, with that found in the free acid. This shows that the excess of lead is not present as an impurity in the form of some other lead salt, since in that case the phosphorus value would have to be less. The excess of lead might be due to the fact that the salt was formed in a strong alcoholic solution, a condition which we know favours the formation of lead salts of the carbohydrates, and that therefore some of the lead might be combined in this way.

The amount of reducing sugar present corresponds to the ratio of one molecule of maltose to one of phosphoric acid (found 61.70, calculated 59.79). The remainder of the molecule, 26.04 per cent, aside from the phosphoric acid corresponds to the empirical formula $C_5H_9O_5$. No evidence for the presence of pentose could be obtained. It was mentioned above that difficulty was encountered in completely burning the sample during combustion owing to the presence of the phosphoric acid. It therefore seems possible that the remainder of the molecule is also a hexose. In view of the fact that it does not reduce Fehling's solution it might be inosite, or, if another molecule of hexose, be still combined with the phosphoric acid in such a way as to destroy its reducing power. Eight grms. of the crude material were examined for inosite, but none could be found, although 60 per cent of the inosite were recovered from phytin treated in a similar way. It is impossible, therefore, to make any definite statement as to the nature of the remainder of the molecule.—*Journal of the American Chemical Society*, xxxviii., No. 2.

MISCELLANEOUS.

Manchester Municipal School of Technology.—The prospectus of the Summer Evening Classes of the Manchester Municipal School of Technology gives full details of the many classes in all branches of engineering, chemical technology, mining, &c., which have been arranged. The fees charged are astonishingly low, but the detailed syllabus shows that the instruction given is by no means elementary in many cases, while it is evidently always thoroughly practical, and aims at giving students a sound and useful equipment for their subsequent work.

The Training of Industrial Chemists.—The Governors of the Huddersfield Technical College, acting with the full approval of the Huddersfield Town Council, have adopted a measure of far-reaching importance to provide additional facilities for training industrial chemists. Following on the large developments undertaken by British Dyes Limited the Governors have decided to establish a new department for specialised study and research in coal-tar colour chemistry (aniline and alizarine dyes), thereby taking a very important step towards meeting both the demand for chemists trained in matters relating to the colour industry and the urgent need for research, in this country, upon matters connected with dye stuffs. The department has been placed under the headship of Dr. A. E. Everest, now Lecturer in Chemistry at University College, Reading, who during recent years has been carrying out a series of important investigations upon colours and plant pigments. Dr. Everest has had some continental experience, having worked both at Zurich and in Berlin. Work will be commenced in September next and the department will provide advanced teaching in matters relating to the production of dyestuffs, colours, and other allied substances. Facilities will be offered for research of all kinds relating to the chemistry of colouring matters. The department will be worked in close connection with the existing departments of chemistry and of dyeing, thereby giving its students the benefits of keeping in touch with the practical application of the products to be dealt with. Spacious laboratories are to be provided, furnished with the most modern equipment and arranged with a view to special attention being devoted to research. It is anticipated that a number of scholarships will be tenable in connection with the department. In addition to day classes for students able to devote the whole of their time to such work, special attention will be given to the training in part-time day and evening classes of youths and men already engaged in the industry, thus giving them the opportunity of becoming skilled workers in the manufacture of colouring matters and intermediate products. The department is being founded with the full concurrence and support of the directors of British Dyes Limited, who are prepared to contribute handsomely towards its establishment.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Rubber Industry.—We shall be much obliged to you if you could kindly let us know if there is any catalogue or book published respecting the names and addresses of chemical manufacturers, and the particular products of each firm. We require this information for the use of our headquarters, the Russian-French India-rubber, Gutta-percha, and Telegraph Works, "Prowodnik," Moscow, Russia, who are occupied with war work for the Russian government. The chemicals regarding which they require particulars are those in connection with the rubber industry.—THE COLUMB TYRE Co., Ltd., 162, Shaftesbury Avenue, London, W.C.

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